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Research Laboratory
of the
Portland Cement Association

BULLETIN 4

Further Studies of
The Bleeding of Portland Cement Paste

BY

HAROLD H. STEINOUR

DECEMBER, 1945

CHICAGO

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Foreword

By T. C. Powers

In July 1939 an extensive paper on bleeding was published -- Bulletin 2 of the Research Laboratory. Although the work behind this paper improved our understanding of the phenomenon, showing bleeding to be a special case of sedimentation, it left open several questions of practical and fundamental importance. Particularly, the theoretically derived equation, which attempted to show the relationship between the various factors controlling the initial rate of settlement, contained an empirical factor that could not be wholly interpreted. This empirical constant seemed to embody the effects of those characteristics other than specific surface which distinguish the behavior of one material from that of another, but there was also the possibility that this constant served to compensate for certain fundamental misconceptions embodied in the equation itself. Consequently, the subject could not be considered closed until something more was known about the significance of this constant.

When Dr. H. H. Steinour joined the laboratory staff in January 1940, he undertook the project of clearing up this question. By much careful and systematic work he has succeeded in increasing our understanding of the bleeding of cement pastes to the point where, so far as additional research is concerned, the subject can be closed until new reasons for continuing the study arise.

In this paper Dr. Steinour's extensive studies of the physical factors that influence bleeding and settlement in general are presented in summary only. Three complete papers on the fundamentals were published in Industrial and Engineering Chemistry (July, September, October, 1944). These papers set forth laws that should

apply to chemical engineering both in and outside the cement industry, particularly to the process of filtering or to thickening by sedimentation.

The present paper sustains the earlier conclusion that specific surface is the most important factor controlling the bleeding characteristics of a portland cement. It goes beyond Bulletin 2 in showing that for cements of given specific surface the bleeding characteristics are controlled by the shape of the particles, by their state of flocculation, and by chemical reactions that occur during the first few moments after the cement and water make contact. It points out also that in abnormal cases bleeding is controlled by the same factors found by William Lerch to control premature stiffening. All these factors are subject to control, although some of them, especially the shape of particle and degree of flocculation, may not be controllable on a commercial scale.

One point made clear by the extended studies is that there is no hope of finding a universal simple formula for predicting bleeding characteristics of a cement from its composition. However, the work provides an understanding of the nature of the variables involved and their effects, and it shows how to test any given material.

On the basis of these studies the writer is now inclined toward the view that if any steps at all are required for the control of the bleeding characteristics of a given cement they should be confined to a regulation of the specific surface of the cement or perhaps to the addition of air-entraining or gas-forming agents; however, neither a change in specific surface nor any addition should be made without a careful study of the effects on all the important properties of concrete. With respect to other factors that influence the bleeding characteristics, it now seems that differences in bleeding characteristics among cements of similar specific surface are not fundamentally of great importance; they

are decidedly secondary to other properties that the manufacturer must control.

In the Introduction to Bulletin 2 (p. 2) the view was expressed that there was an important connection between the bleeding characteristics of the original mix and the durability of concrete when exposed to weathering agencies, and that a reduction in bleeding was in the direction of improvement. This view seemed to be shared at the time by various investigators of concrete, but nothing has developed since to sustain it. On the contrary, some data show that among concretes of relatively low durability those which showed the greatest amount of bleeding gave the best resistance to deterioration by freezing and thawing.

On the theoretical side we have gained a new understanding of the nature of pastes. We now know that a portland cement paste or any other paste of highly concentrated, flocculated particles has a continuous structure which, in the period before hardening, shows some elasticity and much plasticity. At the same time it seems that the articulation of this structure is effected by forces acting across thin layers of water that separate points of near contact between individual particles. The establishment of these two facts makes it possible to understand and explain several aspects of the properties and behavior of fresh cement pastes, especially the plasticity. It also reveals certain current fallacies, particularly the deductions based on a popular but erroneous conception of the flocculated state of cement particles.

Dr. Steinour's work upholds the basic conceptions that were set forth in Bulletin 2 but at the same time shows the need for modifying some of them. For example, the basic equation for the initial rate of bleeding was found to be not wholly consistent with the concept underlying its derivation. Also, the theoretical equation for bleeding capacity was supplanted by an empirical

equation that covers a much wider range in water content than did the theoretical one. Moreover, the theory tentatively put forth in Bulletin 2 concerning the role played by liquid-adsorption was found not to be tenable; instead, the extent of initial chemical reaction was found to be a significant factor.

FURTHER STUDIES OF
THE BLEEDING OF PORTLAND CEMENT PASTE

by Harold H. Steinour

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FURTHER STUDIES OF THE BLEEDING OF PORTLAND CEMENT PASTE

by Harold H. Steinour

Abstract

Results of studies on the bleeding of cement pastes are reported for the period since publication of Bulletin 2 of the P.C.A. Research Laboratory. Basic work on the general problem of the sedimentation of concentrated suspensions is published in more detail elsewhere but is summarized here. On the basis of accumulated evidence, empirical relationships between bleeding capacity and water content of paste are presented which have wider ranges of applicability than the relationship previously assumed. Relationships between bleeding rates and bleeding capacities, and such aspects as the effect of cement fineness and the duration of bleeding are also discussed. Bleeding data for a number of cements are compared with other properties of the cements, and correlation between the rate and amount of bleeding and the early chemical reactivity of the cement is shown. Miscellaneous test data which indicate that bleeding rate and bleeding capacity are subject to many influences are presented. A method of conducting the bleeding test is outlined as an appendix. The report deals only with the bleeding of pastes, not mortars or concretes.

Introduction

This report is supplementary to Bulletin 2 issued by the Research Laboratory of the Portland Cement Association in 1939 under the title, "The Bleeding of Portland Cement Paste, Mortar and Concrete," by T. C. Powers.

In the interim, the studies of bleeding have been continued and numerous tests have been made both on cement pastes and on concretes. In addition, tests have been made on suspensions of other solids, in further investigation of theoretical aspects.* The present report reviews the general implications of this recent work with respect to the bleeding characteristics of cement pastes.

The bleeding of a cement paste may be described as the development of a layer of water at the top of the paste as a result of the settlement of the cement particles. The type of testing employed in the work covered in Bulletin 2, and in that which has been done since, consists in obtaining a time record of the level of the paste at the center of a wide vessel. The observations are made with a micrometer microscope by sighting on a "float" which remains at the paste-water boundary. Practical details supplementing those given in Bulletin 2 will be found in Appendix E.

Most of the cements for which data are reported have been given either the group identification SBR or LTS. The cements in both groups were produced from commercial clinker and nearly all of them were ground in commercial mills. Chemical compositions are given in Appendix A. The letters relate solely to the research purposes for which the cements were originally obtained. They stand for Special Basic Research and Long-Time Study.

Most of the data given in this report for cements of the SBR group were obtained under a program of basic research supervised by T. C. Powers. Early studies by William Lerch supplied the first evidence for some of the chemical effects. Data obtained from W. C. Hansen

*A part of this work is published in Industrial and Engineering Chemistry under the title "Rate of Sedimentation." See references (14), (15) and (16). The papers have been reprinted as Bulletin 3 of the Research Laboratory of the Portland Cement Association.

on cements of the LTS group were utilized in the general comparison of bleeding characteristics and other properties of cements. Most of the bleeding tests were made by Robert H. Borkenhagen, Lynn A. Brauer, Richard G. Bruschi, Frank Rosal, Herbert W. Schultz, and Edwin M. Wiler.

1. The Dormant Period

It was found experimentally and was reported in Bulletin 2 that for a considerable time after a neat cement paste is mixed and placed in a deep, wide vessel the rate of subsidence of the paste at the center of the vessel remains strictly constant (as nearly as can be judged from readings accurate to 0.001 mm and timed to 1 second). With the initial paste heights of 4 to 8 cm that were commonly used, the constant-rate periods sometimes lasted 30 minutes or more. A special test indicated that under suitable conditions the constant rate could be maintained for 75 minutes. It was observed, also, that the bleeding capacities, or total settlements expressed as proportions of the initial heights of paste, were independent of the initial heights for total bleeding times up to 75 minutes. Consequently, it was concluded that for 75 minutes most cements show little chemical reactivity and may be considered to be in a dormant state, at least as far as effects on bleeding are concerned. (See Bulletin 2, pp. 74, 84.)

As a part of the subsequent work, further tests were made to determine the maximum periods during which various cements would maintain constant bleeding rates. The final estimates were obtained from bleeding tests made in cylinders 9 cm in diameter, filled with cement paste to a depth of 28 cm. Five cements of average fineness, representing different clinkers, were tested in this way. For two of the cements, wall-resistance appeared to be negligible and the test consisted simply in determining for how long the initial constant-rate period was actually maintained. In the other cases a change from the initial to a slightly lower rate occurred after 20 to 40 minutes. This second rate remained

practically constant for a considerable time and then gradually diminished. The change from the one constant rate to the other, slightly lower one was thought to be caused by wall resistance since, in preliminary tests in a considerably narrower cylinder, more such changes were often clearly evident. It was concluded that the successive constant rate periods should be added together to estimate the time for which a single constant rate might be maintained in the absence of wall effects; for the same cements this gave about the same results irrespective of whether the wide or narrow cylinder was used. Fortunately, the two extremes of the range in dormant periods were found in those tests in which no allowance for wall resistance was needed. The results for the tests in the 9 cm-dia. cylinder are shown in Table 1.

In the preliminary work with the narrower cylinder, cements of widely varied fineness (a series for each clinker) had been tested and had shown no large or consistent effect of fineness on the duration of the dormant period. Apparently, most cement pastes prepared as in these tests can maintain, under suitable conditions, remarkably constant bleeding rates for periods of $2/3$ to 2 hours.

A somewhat different approach to the study of the dormant period was adopted in other tests, in which pastes of a given concentration were allowed to stand after mixing, for intervals of successively increased length, and were then briefly remixed and tested for bleeding at paste heights of only a few cm, as in the usual bleeding tests. Data on the most extensive test of this kind are shown in Table 2. The cement used to obtain the data of Table 2 had shown, in tests in the tall 9 cm-dia. cylinder, a dormant period of about 60 minutes. This agrees in part, at least, with the data of the table in that the bleeding rate apparently first began to be reduced significantly in the test that was begun after the 60-minute rest period. The table is believed to show in a rather striking way the constancy

Table 1

Estimated Dormant Periods and Other Data
for Tests on Pastes 28 cm High, in Cylinders
9 cm in Diameter, at 23.5°C

Times are figured from the end of a 7-minute mixing schedule:

2' mix - 3' wait - 2' mix.

The proportions of water in the pastes were 0.575 to 0.600 by absolute volume.

The bleeding rates in millionths of a cm per sec were 125 to 150. No channels or boils developed.*

Cement Lot	Clinker Ref. No.	Total** Spec. Surface (Wagner Turb.) cm ² /gm	No. of Const. Rate Periods	Apparent Dormant Period, min.	Total Bleeding Time, min.
SBR-15365	1	1665	2	60	116
SBR-15496	2	1740	1	40	81
SBR-15621	3	1820	2	60	131
SBR-15668	4	1830	1	115	205
SBR-15697	5	1705	2	90	161

*For the purpose of minimizing wall resistance, faster bleeding pastes obtained by increasing the water contents would have been preferable. It was found, however, that, because of the heights used, pastes having greater water contents were susceptible to channeling.

**This is the value obtained by the A.S.T.M. method, plus an estimate for the surface area of the residue on the 325-mesh sieve.

Table 2

Bleeding Tests on Remixed Pastes

Cement LTS-21

Water content of paste: 0.601 by absolute volume

Initial mixing schedule: 2' mix - 3' wait - 2' mix

Final mixing: $\frac{1}{2}$ min.

Height of paste: 36 mm

Temperature: 23.5°C

Results for remixed pastes are averages of 2 or 3 tests.

Rest Period, min.	Bleeding Rate, Q, cm per sec, $\times 10^6$	Bleeding Capacity, $\Delta H'$	Duration of Const. Rate Period, min. (Approximate)	Duration of Bleeding, min.	Time between Initial Mix and End of Bleeding
0	194	0.122	20	55	55
15	189	0.113	18	55	70
30	196	0.125	15	57	87
45	192	0.106	17	52	97
60	185	0.103	18	48	108
90	172	0.090	20	47	137
120	167	0.075	12	45	165

Symbols used conform to those of Bulletin 2. See also the nomenclature list at the end of this report.

with which bleeding properties can be maintained for a considerable time.

Though the period during which a constant bleeding rate can be maintained has been called the dormant period, it appears from other data that chemical reactions are not strictly in abeyance during this time. A discussion of how these different aspects may be reconciled is given at the close of the next section.

2. The Initial Bleeding Rate and Its Theoretical Significance

The Rate Equation of Bulletin 2

In Bulletin 2 much of the theoretical analysis relates to the initial period of constant bleeding rate. It was assumed that during this period the cement particles in the top layer of the paste maintain the arrangement and spacing that results from the mixing, and that opposition to the settlement of these particles is caused only by the viscous resistance of the free water in the spaces between particles. By analogy to the work of Fair and Hatch (7) and of Kozeny (9) and Carman (4,5) on viscous flow through granular beds, it was further assumed that the flow of the water between the settling particles conforms to Poiseuille's law for capillary flow, as adapted to non-circular channels by use of the hydraulic radius.* By employing these assumptions, using a proportionality constant determined empirically by Carman, an equation for the initial constant rate of bleeding was derived. When all the water in the paste is assumed to take part in the flow between the particles, the equation takes the following form:

$$Q = \frac{0.2}{\sigma^2} \cdot \frac{g(d_c - d_f)}{\eta} \cdot \frac{w^3}{c} \quad (1)**$$

*The hydraulic radius may be defined as the ratio of the **volume** of moving fluid to the area of the surfaces wetted by that fluid.

**This is the expanded form of Equation 14 of Bulletin 2 when $w_i = 0$.

where:

- Q = the rate of bleeding, cm of subsidence per second
 g = the gravitational acceleration, cm/sec^2
 d_c = density of cement, gm/cm^3
 d_f = density of the water, gm/cm^3
 η = viscosity of the water, poises
 σ = specific surface of cement, cm^2/cm^3
 w = volume of water per unit volume of mix
 c = volume of cement per unit volume of mix
($c + w = 1$)

Actually, to obtain agreement with the data of Bulletin 2, Powers found it necessary to modify Equation 1 as follows:

$$Q = \frac{0.2}{\sigma_w^2} \cdot \frac{g(d_c - d_f)}{\eta} \cdot \frac{(w - w_1)^3}{c} \quad (2)^*$$

where the specific surface in sq cm per cu cm is here written as σ_w to indicate that it was determined by the Wagner turbidimeter method, and

w_1 = a constant for tests on a given cement at a given temperature, which, since it is subtracted from w , was assumed to represent a quantity of immobile water per unit volume of paste.

The empirical constant, w_1 , was found to have different values for different cements, but it was always of such size that had it not been introduced the estimated bleeding rates would have been much too high, often 6 or 7 times the actual rates. Since the physical significance of the term remained largely a matter of speculation, the need for w_1 constituted a weak link in

*Same as Equation 14 of Bulletin 2.

the evidence supporting the theory of bleeding that had been developed.

Water of hydration was an insufficient explanation of w_i , for a w_i term was needed also in representing data obtained for pastes of cement and kerosene, and for other inert systems. The possibility of stagnant liquid was considered but seemed to be ruled out by the work of Carman (4,5), who found no need of a w_i term in analyzing the flow of liquid through beds of particles (of low specific surface). The explanation of w_i that was tentatively offered in Bulletin 2 was developed in terms of adsorption of liquid by the solid. Though this explanation agreed with views of von Buzagh (3) (who was quoted), there are other investigators who believe that adsorption layers of the thicknesses necessary to account for the w_i values are not possible (1,2). It is also to be noted that the magnitude of w_i is independent of the quantity of cement in unit volume of paste. This fact is somewhat difficult to reconcile with the interpretation of w_i simply as the quantity of adsorbed water per unit volume of paste.

Further work on the nature of w_i seemed advisable both for its bearing on the theory and for the insight which it might give with respect to the different bleeding tendencies shown by different cements. The three papers that have since been written on "Rate of Sedimentation" (14,15,16) show how the problem was attacked through work on simpler systems. Here only a brief survey of some of that work will be given.

Basic Studies on Rate of Sedimentation

Work with uniform spheres in the disperse, or non-flocculated, state showed that for concentrated suspensions of the spheres the following rate equation was satisfactory:

$$Q = \frac{0.246}{\sigma^2} \cdot \frac{g(d_c - d_f)}{\eta} \cdot \frac{w^3}{c} \quad (3)$$

where the symbols have the same significance as given previously. except that "solid" and "fluid" should be read in place of "cement" and "water". It will be noted that this equation conforms to Equation 1 except for the value, 0.246, of the empirical proportionality constant. It therefore indicates substantial agreement of the basic theory of Bulletin 2 with data for uniform, non-flocculated spheres.

However, to obtain agreement with data for a set of tests on chemically inert, uniform-size, angular particles in non-flocculated suspension the equation had to be changed to

$$Q = \frac{0.36}{\sigma^2} \cdot \frac{g(d_c - d_f)}{\eta} \cdot \frac{(w - 0.168)^3}{c} \quad (4)$$

That is, not only was a term needed like the w_i of Equation 2 but the constant 0.246 had to be replaced by 0.36.

By assuming immobile liquid, it was possible to account for both changes. Any immobile liquid in a non-flocculated system, such as was under study, would be located at the individual particles of solid, and the quantity per unit volume of the suspension would presumably be proportional to the solid content, c . Correction for such immobile liquid, represented as $\frac{w_i}{1-w_i} c$, transforms Equation 3 to

$$Q = \frac{0.246}{(1-w_i)^2 \sigma^2} \cdot \frac{g(d_c - d_f)}{\eta} \cdot \frac{(w - w_i)^3}{c} \quad (5)^*$$

if use is made of the fact that $c = 1 - w$. When $w_i = 0.168$, the factor $\frac{0.246}{(1-w_i)^2}$ amounts to 0.356. Hence,

Equation 5 as applied to the systems under study shows excellent agreement with Equation 4. The assumption of

*The immobile liquid is subtracted from w and added to c , because in Equation 3 the w and c represent, respectively, the mobile and immobile parts of the system. See also Appendix C.

immobile liquid proportional to c is thus wholly adequate to explain the results, and because of the simple nature of a non-flocculated suspension of uniform-size particles the possibility that there may be other equally satisfactory explanations seems small.

Experiments with different-size particles, and study of published work, led to the conclusion that in non-flocculated suspensions of inert particles the magnitude of $\frac{w_i}{1-w_i}$ is independent of particle-size and dependent solely on particle shape.

The results of the work on non-flocculated suspensions may be summarized as follows: In a non-flocculated suspension of approximately uniform-size particles the basic theory that led to Equation 1 is well supported when the particles are spheres, for the data agree with the equation except for the value of the proportionality constant which is, after all, empirical. When the particles are angular, they apparently carry with them a quantity of liquid which, per unit volume of the suspension, is proportional to the volume of solid and independent of particle-size. The large quantity of the liquid involved, its invariance with respect to the degree of subdivision of the solid, and its dependence on particle shape are considered to be strong indications that the liquid is not bound to the particles but simply remains stagnant at angularities in their contours. That is, the sharp angularities of the particle-surfaces apparently give rise to dead spaces where the liquid remains relatively immobile.

In Bulletin 2, stagnant liquid was not assumed because Carman had found no indication of it in studies on flow through uniform granular beds. The experimental results discussed here appear to demand this assumption, but even if the original explanation of w_i in terms of adsorbed liquid could still be made, it would no longer avoid disagreement with results obtained by Carman for granular beds, for Carman has now reported work with

fine powders (6) and has in general found no need to assume an appreciable adsorption. Apparently, flow of liquid past suspended particles is not as strictly analogous to the flow through the compact beds investigated by Carman as was at first thought. This is indicated also by the change in the proportionality constant of the rate equation.

In the further course of the investigation of rate of sedimentation, tests were made on flocculated suspensions of the same angular particles that had been tested when not flocculated. Equation 5 was still found to apply, to a good degree of approximation, but the value of w_1 was greater than before. That is, the suspensions settled more slowly when flocculated. Two possible explanations are seen for the increase in w_1 : (1) The quantity of stagnant liquid may be increased by reason of interparticle contacts caused by the flocculation. (2) There may be small isolated pockets of liquid distributed through the flocculated mass. Such pockets might contribute to the value of w_1 in approximately the same way as stagnant liquid. That is, liquid removed from the floc-space in this way would lower the proportion of water in the latter, and the correction term would be of the same form as for water that is stagnant at the individual particles.*

Many different powders, each containing a wide range of particle-sizes, were tested as flocculated suspensions. Most of them showed fair agreement with Equation 5, thus demonstrating that agreement with the equation was not dependent upon maintenance of a uniform size of particle.

To test directly the assumption that only the viscous resistance of the water opposes the fall of the flocculated particles during the constant-rate period, a number of tests of hydrostatic pressure were made, principally on cement pastes. The results agreed fully with the assumption.

*See brief explanation in the second article on "Rate of Sedimentation" (15).

Comparison of Rate Equations

Attention needs now to be directed to the fact that Equation 5, which was developed from this basic study, is not strictly the same as Powers' Equation 14, which is represented by Equation 2 of this report. This might lead to the supposition that cement pastes do not behave like these other flocculated suspensions. However, it has been found (16) that for cement pastes Equations 2 and 5 give results that agree within the limit of error of the data. Evidently, therefore, the cements act like the majority of the other powders, and the ideas that have been developed regarding the significance of w_i are as applicable to the cements as to these other powders.

As a result of the studies just discussed, Equation 2 as applied to cement pastes is now regarded simply as an approximate version of Equation 5, in which a constant times σ_w is used in place of the more accurate σ , and $\frac{1}{(1-w_i)^2}$ is represented by an average value appropri-

ate to the particular limited range of w_i values found for cements. Since the approximations seem to be no greater than is justifiable in practical work, and since they simplify both the experimental work and the computations and give results directly comparable with those in Bulletin 2, Equation 2 was used for the determination of all values of w_i for cements that are cited later in this report. Indeed, accurate values of σ necessary for a strict application of Equation 5 were not available for these cements.

Probable Causes of Differences in the Bleeding Rates of Different Cements

The contributions to the w_i values that have been discussed thus far may be considered to be wholly of physical origin, for the studies were made on chemically inert systems. In such systems, as has been seen, the magnitude of w_i is apparently determined by the particle shape and by the state of flocculation. In cement paste,

however, it seems doubtful whether the differences in particle-shape are sufficient to contribute importantly to the differences in the w_i values. The cement pastes may differ somewhat in the magnitudes of their flocculating forces, but, again, it is doubtful if the w_i values are much affected. The cement pastes are all flocculant, and when channeling is avoided, the value of w_i is not sensitive to moderate differences in the strength of flocculation. This is indicated by the studies on silica powder that are reported in Bulletin 2 (p. 72). Values of w_i do vary markedly with one physical property of cements, namely, the fineness. However, tests on flocculated suspensions of inert powders (16) showed little effect of fineness on w_i when the powders were composed of many different sizes of particles, as are portland cements; therefore, the differences in the w_i values found for cements are probably mainly a result of chemical reaction.

Indeed, if significant amounts of reaction products form as coatings on the cement particles during the mixing period, the different reactivities of different cements provide a ready explanation for all the differences in w_i values. Such coatings would increase the immobile phase at the expense of the mobile one, and this would increase w_i . Moreover, under the assumption that the thickness of the coating would not vary much with the fineness of the cement, the volume of the immobile phase would increase with the fineness, thus accounting for the increase in w_i with fineness.

Arguments that were advanced in Bulletin 2 (p. 56) against the assumption that there is appreciable formation of reaction products before the end of the dormant period now appear less forceful as a result of the subsequent studies. The proportionality constant of the rate equation is no longer considered to be maintained so precisely at just the same value for different cements as was formerly thought. Neither Equation 2 nor Equation 5 is so precise a representation of the data for cements

as to rule out the possibility that an appreciable formation of reaction products occurs during the mixing period. Indeed, the necessity for a long and vigorous mixing (see Bulletin 2, p. 135) can be regarded as support for the assumption that a significant amount of initial reaction does take place. The initial reaction need not cease entirely after the mixing period, for a reaction layer initially formed loosely over the particles could fill in without altering the bleeding rate. Also, any reaction product that was formed in, or swept into, the small, stagnant spaces that are apparently to be found at angularities in the particles would have no effect on the rate. Heat-data, illustrated by Fig. 1, are consistent with the views on chemical reaction that have just been stated. Microscopic observations also give some indication that a film of hydration product does form (10). Such coatings need not be more than a few tenths of a micron in thickness in order to account for the differences in the w_i values. The dependence of bleeding characteristics upon specific chemical factors will be considered in later sections of this report.

Because of the changed conception of the significance of w_i , the original definition of this term needs modification. Even when stagnant water and water of hydration are wholly responsible for w_i , the quantity of such water per unit volume of paste is not equal to w_i but to $\frac{w_i}{1-w_i}$ c. Because of this, and also because any

water in "pockets" contributes to w_i in a different way, the term does not represent one simple physical entity. It can be defined as a correction for liquid that is not involved in the flow, but it cannot be considered to represent, directly, the quantity of such liquid.

Fig. 2 shows the ranges in bleeding rates that are likely to be found at various water-cement ratios when cements are of ordinary, but somewhat variable, fineness and show the usual variations in w_i .

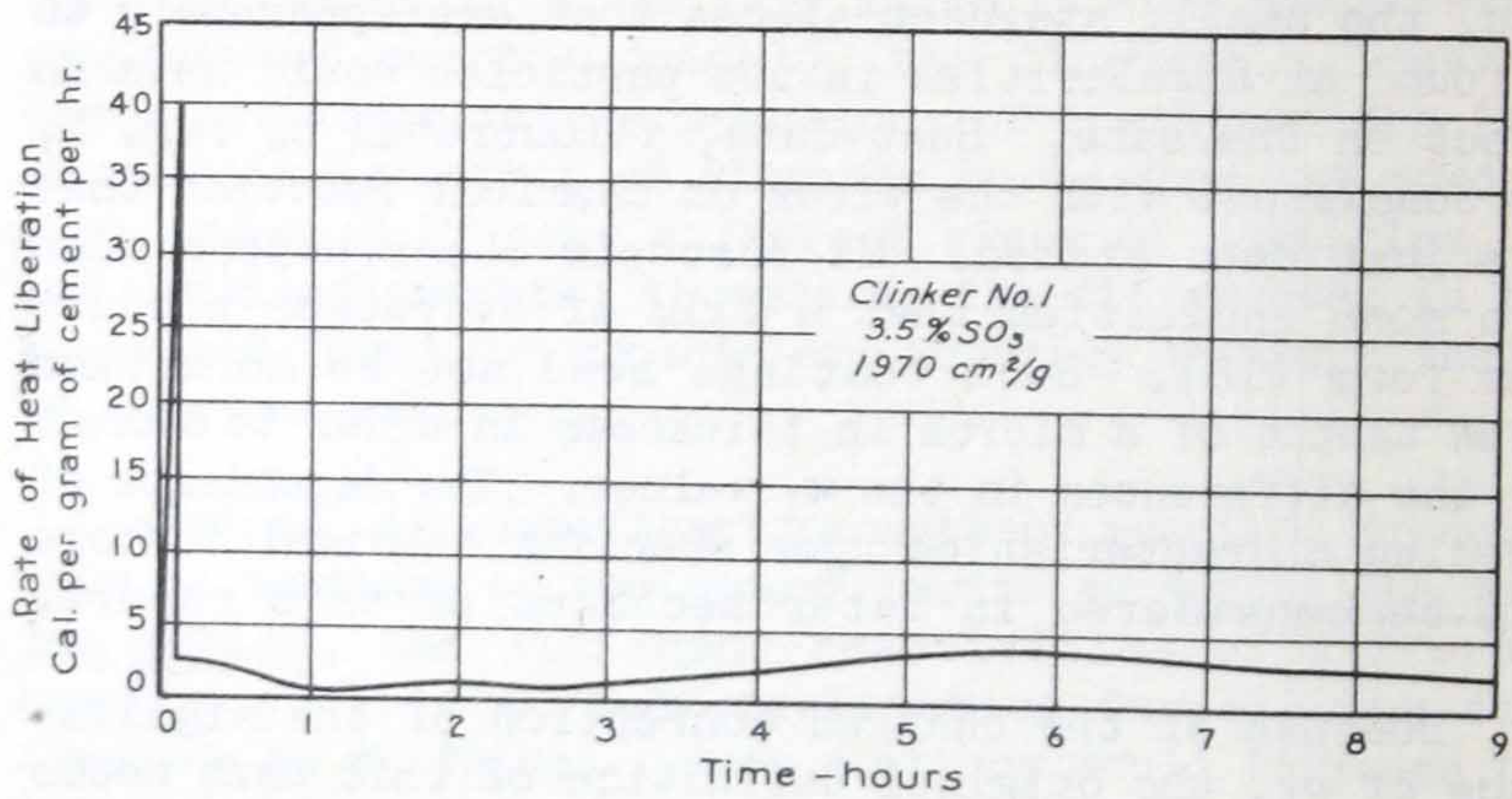


Fig. 1 - Rate of Heat Liberation of Cement Paste versus Time

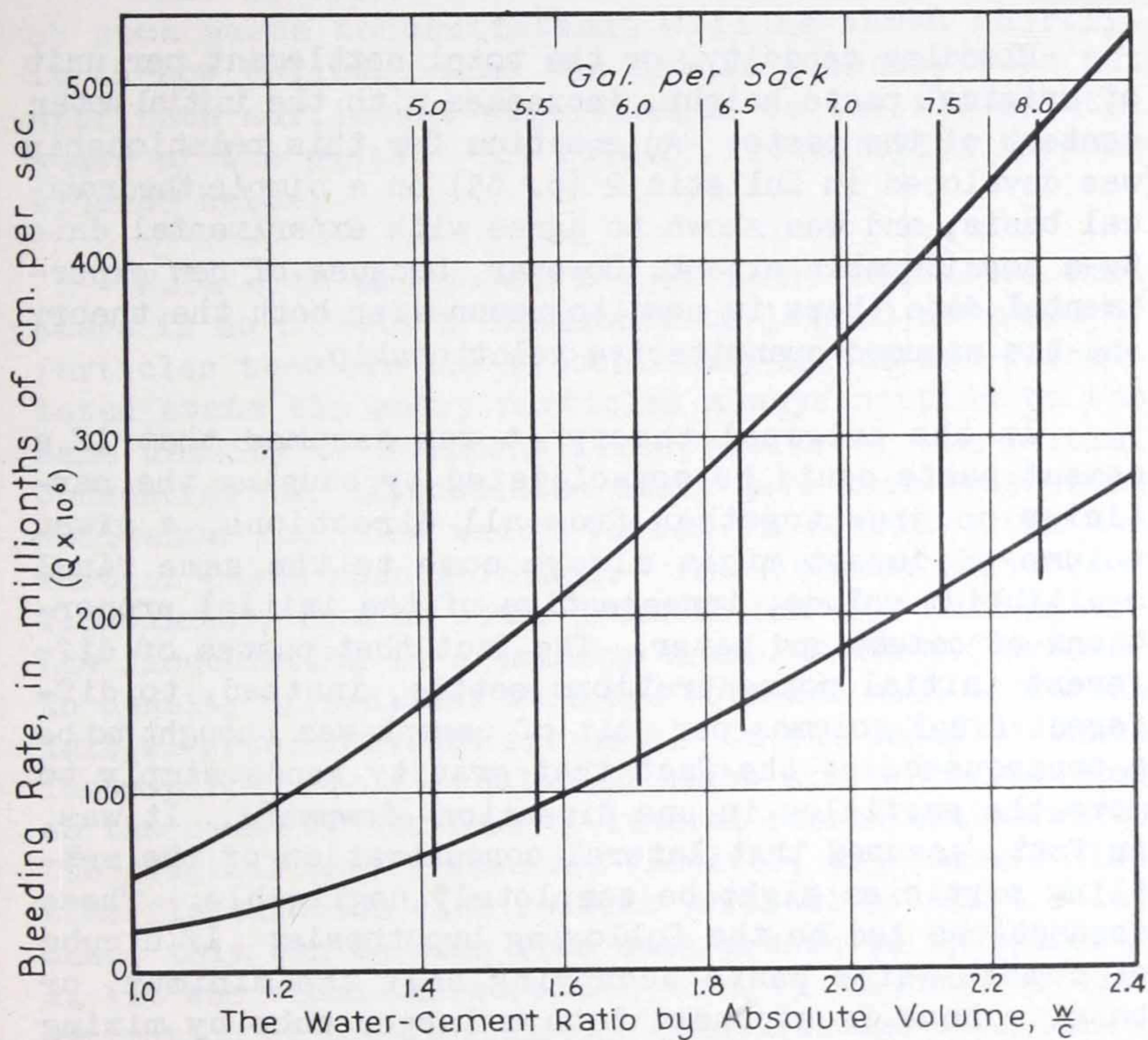


Fig. 2 - Ranges in Bleeding Rates

Most cements with specific surfaces of 1850 ± 100 sq. cm. per gm. will give pastes whose rates of bleeding fall within the band shown. The different rates found for different cements are attributable to differences in chemical constitution and in treatment as well as to differences in fineness.

3. The Bleeding Capacity Considered in Relation to Water Content of Paste

Theoretical Aspects

Bleeding capacity, or the total settlement per unit of original paste height, increases with the initial water content of the paste. An equation for this relationship was developed in Bulletin 2 (p. 65) on a simple theoretical basis, and was shown to agree with experimental data to a considerable extent. However, because of new experimental data there is need to reconsider both the theory and the assumed quantitative relationship.

In the original theory it was assumed that if a cement paste could be consolidated by causing the particles to draw together from all directions, a given volume of cement might always come to the same final equilibrium volume, irrespective of the initial proportions of cement and water. The fact that pastes of different initial concentrations settle, instead, to different final volumes per unit of cement was thought to be a consequence of the fact that gravity tends simply to move the particles in one direction--downward. It was, in fact, assumed that lateral concentration of the settling particles might be completely negligible. These assumptions led to the following hypothesis: If a cube of cement-water paste occupying only the minimum, or base, volume is expanded into a larger cube by mixing with additional water, the resultant paste will settle until its height is the same as that of the original cube.

On the basis of this hypothesis, Equation 30 of Bulletin 2 was developed, in terms of bleeding capacity and "excess" water. As shown in Appendix D, the corresponding relationship between the bleeding capacity and the proportion of cement in the initial paste is

$$c = c_B(1 - \Delta H')^3 \quad (6)$$

where c_B is the volume of cement per unit of the base volume.

That Equation 6 has been found to be unsuitable at some paste concentrations will be shown shortly. It is now believed that the original theory does not attribute sufficient significance to the flocculated state of the paste. The role of flocculation is considered below.

Work with emery powders (15) has indicated that there is no effective hinderance to lateral movement of particles that are not flocculated; in the non-flocculated state the emery particles always settled to the same density of sediment irrespective of the initial concentration. Flocculated emery gave much less dense sediments and ones which varied in density with the initial paste concentration. Since cement pastes are flocculated, it also seems probable that for such pastes the flocculation is a primary cause of the differences in density of sediment that are obtained when different initial water contents are used. On the basis of these facts alone, the flocculation might simply be regarded as the cause of the lack of lateral consolidation which the original theory assumes. However, experiments show that flocculation also reduces vertical movement. Indeed, this can be seen from data presented in Bulletin 2. It was shown there (p. 72) that by varying the concentration of the flocculating agent (though still maintaining flocculation) a large change in the bleeding capacity of a suspension of silica powder can be produced even though the initial concentration of silica is maintained constant.

To take cognizance of this fact while maintaining the original theory it is necessary to assume that the size of the base volume is dependent upon the strength of the flocculating forces. Evidently, the original flocculated structure must be assumed to yield rather easily under the action of gravity up to a certain point and then to yield no more even though a more compact

arrangement could be produced if the flocculating forces were absent. This, in itself, is indeed probable, for it seems to be required by other considerations also, such as the fact that the bleeding capacity is practically independent of the original height of the paste. Up to this point the discussion leaves the original theory intact, but it shows that the flocculated state of the paste is important and must be taken into consideration. To some extent the influence of flocculation seems to fit in with the theory of Bulletin 2, but other aspects of flocculation discussed below suggest that the original theory is too simple.

At concentrations at which there is no channeling there is evidently insufficient water to permit the floc to form at its loosest possible texture; apparently, therefore, a network forms throughout the whole space. The cement particles, which make up this structure, are presumably held close* to their nearest neighbors (in the filaments of the network) by the forces of flocculation, so that there could apparently be but little settlement if some parts of the structure did not move sideways. Perhaps the readjustments are such that lateral movements are of secondary importance relative to vertical movements, but the flocculated nature of the paste makes it seem unlikely that sideward movement can be neglected entirely. This viewpoint, together with the fact that Equation 6 strictly represents the theory of purely vertical motion only for certain initial arrangements of the particles,** has led to a more empirical study of the data.

*In their equilibrium positions the particles are probably still separated by films of liquid, but they are so close together as to appear to be in actual contact when observed under the microscope.

**A "staggered" arrangement of the particles in Fig. 16 of Bulletin 2 would lead to a significantly different result.

Empirical Relationships

The direct experimental relationship between bleeding capacity and initial water-content that has been found for pastes made from cements of medium fineness is shown by Fig. 3. The tests that are represented were conducted over a much wider range in water content than that originally employed in testing the theory advanced in Bulletin 2. The range is also much greater than that used in cement practice. This was intentional since a primary purpose of the tests was to see whether the bleeding capacities for all possible concentrations could be represented by one equation. The curves that have been drawn through the data-points are parabolic, and become tangent to the w-axis at the vertices of the parabolas. These curves are believed to represent the data rather well, except at the highest values of w for cement 15341.

To see how these parabolas compare with Equation 6 it is convenient to use plots of $(1 - \Delta H')^3$ versus c in which Equation 6 gives straight lines through the origin. Such plots are shown in Fig. 4. The parabolic curves of Fig. 3 give the S-shaped curves of Fig. 4, which are in reasonable agreement with the data. The straight lines corresponding to Equation 6 obviously represent only a part of the data. Discrepancy at the lower concentrations begins well within the normal bleeding range, at values of w below those at which channeling occurs, and within the range used in commercial practice.

The parabolic curves of Fig. 3 become straight lines when $\sqrt{\Delta H'}$ is plotted against w. Fig. 5 shows such plots both for the cements of Fig. 3 and for a series of cements which vary in fineness. The straight lines must all pass through the point (1,1) since the bleeding capacity, $\Delta H'$, must equal 1 when $w = 1$. This aspect is of practical value since it means that when the assumed relationship is applicable the trend line can be established from one good experimental point. However, it is evident from Fig. 5 that cements finer than about 1700

sq cm per gm cannot be relied upon to conform to the assumed relationship at values of $\sqrt{\Delta H'}$ of 0.2 or less ($\Delta H' = 0.04$ or less).

In contrast with this it has been found that the bleeding capacities of nearly all cements, even ones having specific surfaces as great as 2400 sq cm per gm, can be represented adequately by a straight line on a plot of $\sqrt{\Delta H'}/c$ versus w/c if values of w/c are restricted to ones below 2.6* (w below 0.72). Since this limit corresponds to almost 9.5 gallons of water per sack of cement (a water-cement ratio of 0.81 by weight), the practical range is covered. Fig. 6 shows that this method of plotting is satisfactory for all cements of Fig. 5. The plot of $\sqrt{\Delta H'}/c$ versus w/c has been tried with 26 cements of medium fineness (1600-2000 sq cm per gm), 6 cements of lower fineness, and 8 cements of higher fineness (above 2200 sq cm per gm). Only two cements, ones having specific surfaces above 2500 sq cm per gm, gave data that could not be represented adequately by the linear relationship. For these, the bleeding capacities were relatively too high at values of w/c of 1.5 and less, if the line was drawn to represent the other data.

*At values of w/c above 3.5 a closely linear relationship exists between the first powers of $\Delta H'/c$ and w/c . The complete curve of $\Delta H'/c$ versus w/c has some aspects of a hyperbola, but below $w/c = 1.5$ the change in slope is more gradual than the hyperbolic curve fitting the upper points. It is of incidental interest that if the data are plotted as $\Delta H'$ versus w/c , as was done for Fig. 17 of Bulletin 2, they can be represented very well by a straight line over a considerable range in w/c , but at values of w/c above 3.5 this relationship fails. It also does not adequately represent the data at the lowest values of w/c . However, the linear relationship is satisfactory over a much wider range in w/c than are the curves of Fig. 17 of Bulletin 2.

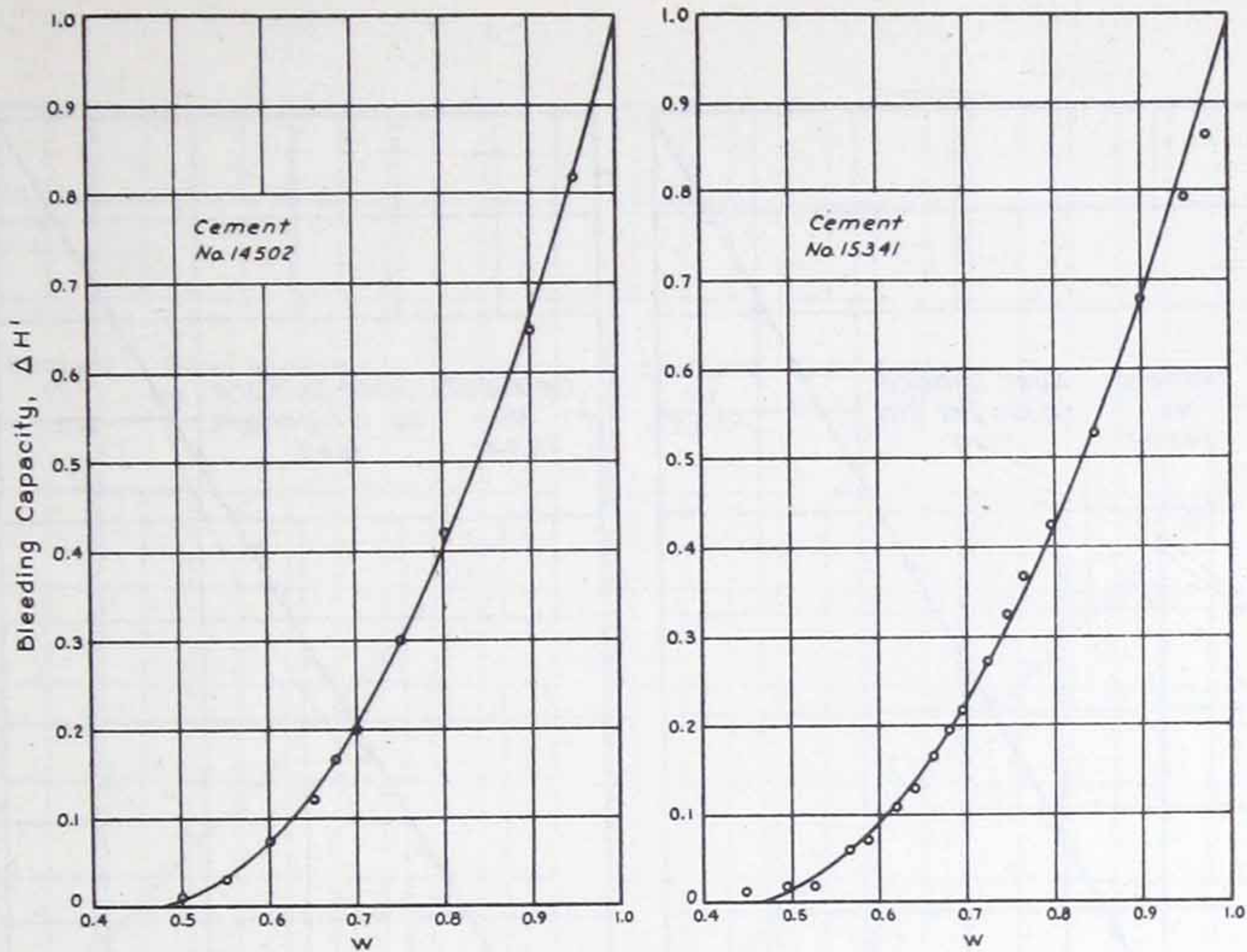


Fig. 3 - Bleeding Capacity versus Water Content for Cement Pastes of All Possible Concentrations

The curves shown are parabolic.

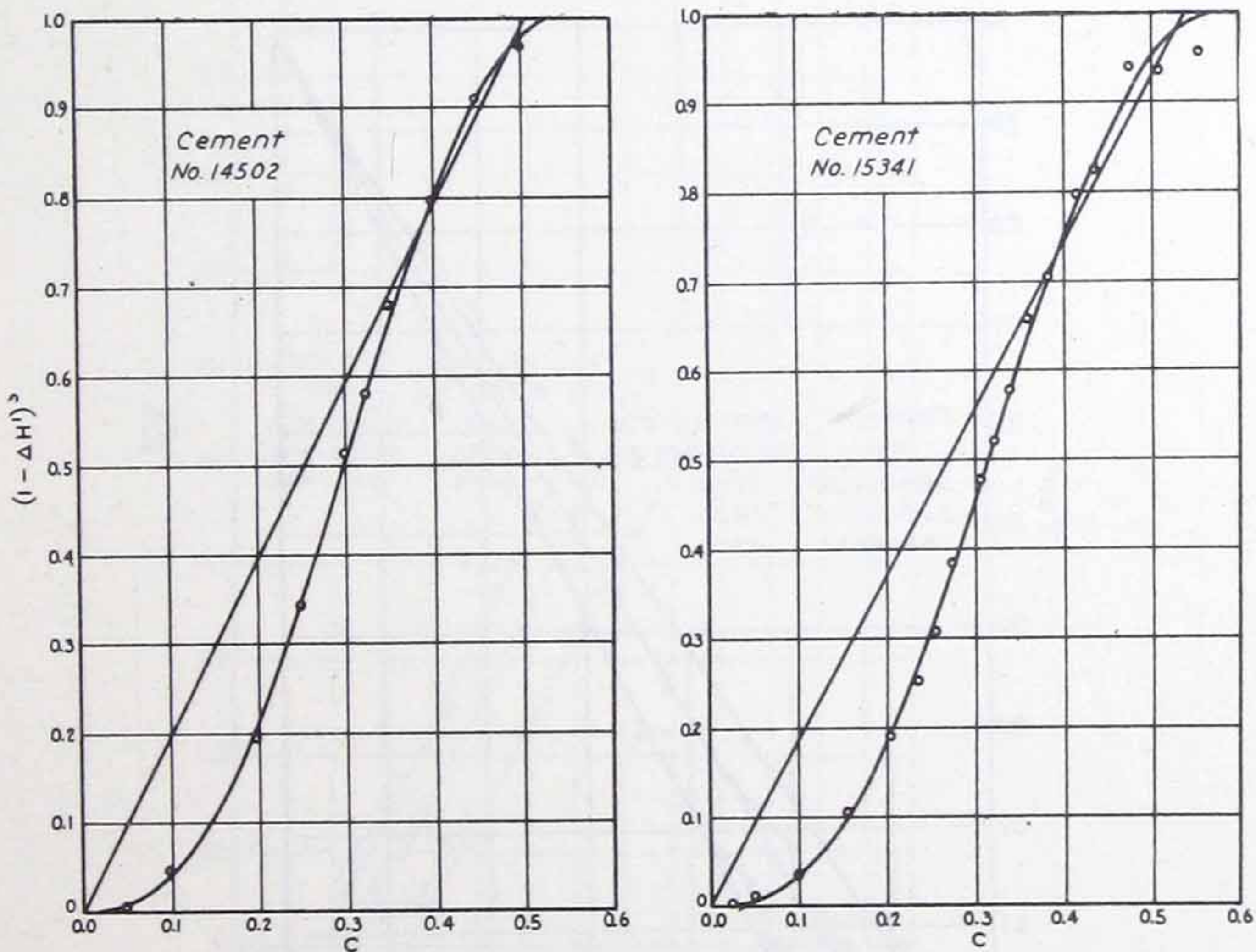


Fig. 4 - Comparison of Different Ways of Representing Bleeding Capacity Data

The straight lines represent Equation 6. The S-shaped curves correspond to the parabolic curves of Figure 3.

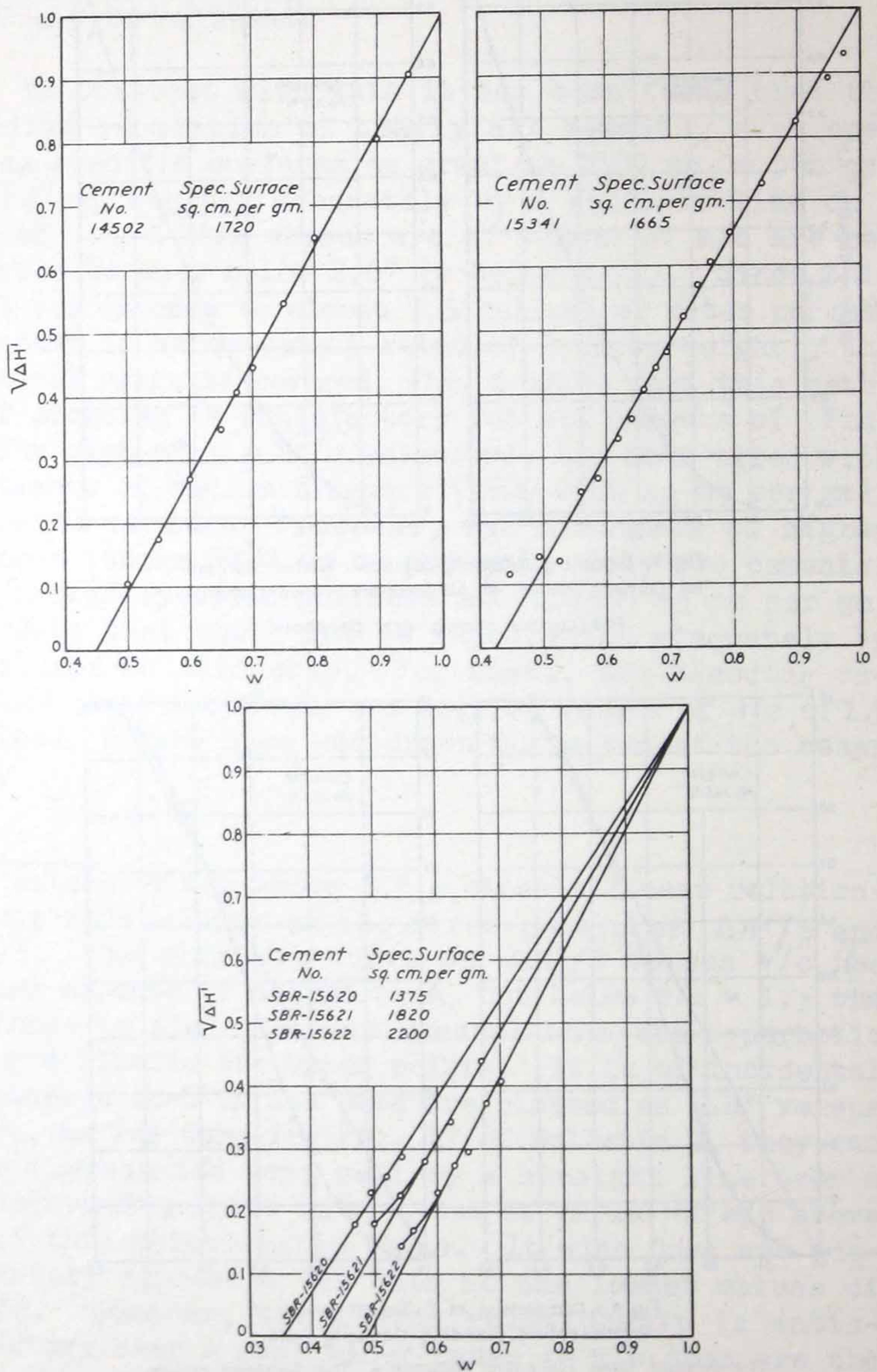


Fig. 5 - Plots in which the Data Conform to Straight Lines if the Relationship Between Bleeding Capacity and Water Content Is Parabolic $\sqrt{\Delta H}$ versus w

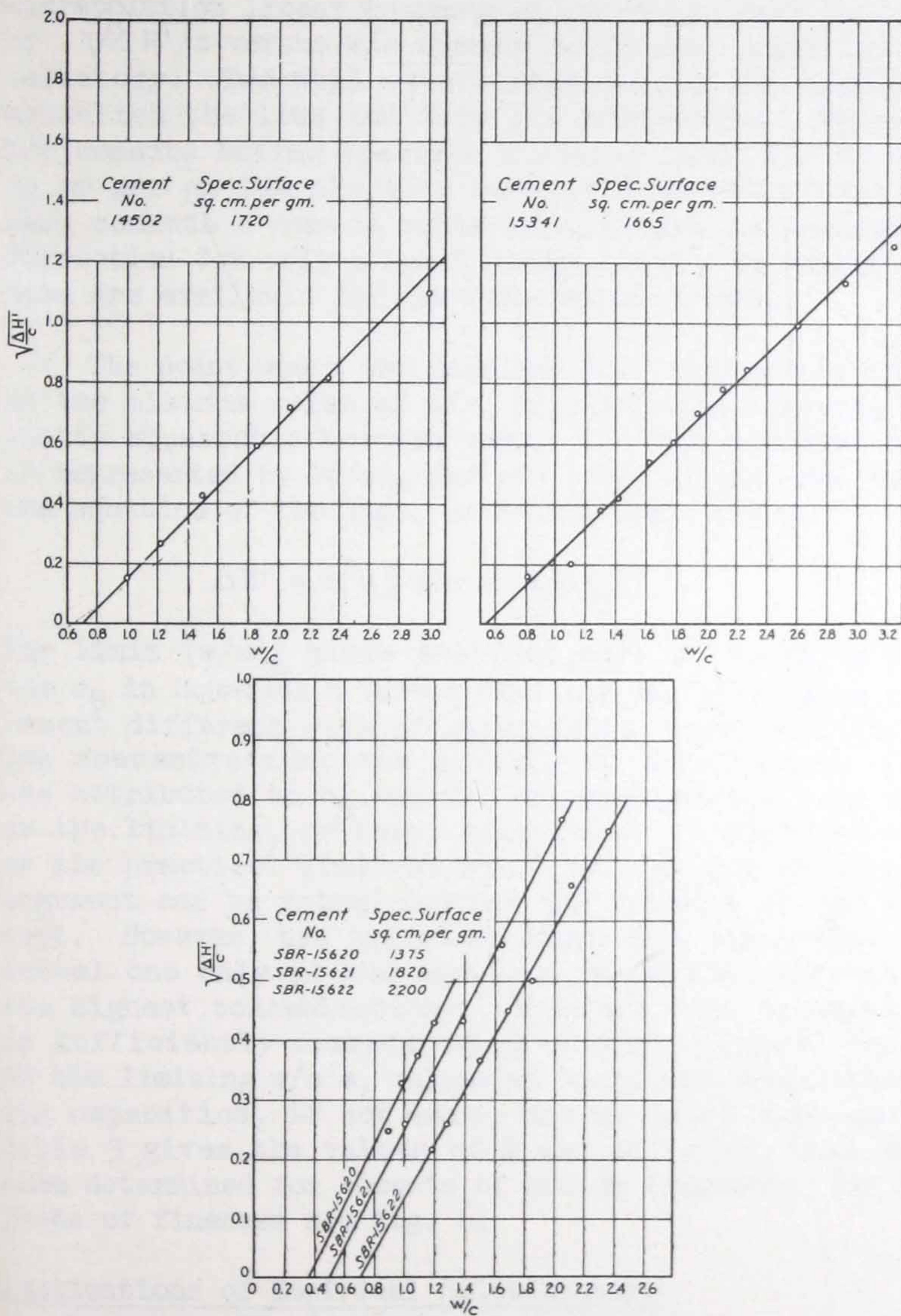


Fig. 6 - A Method of Representing Bleeding Capacity Data Linearly That Is Applicable to Cements of Practically All Finenesses within the Practical Range of Paste Concentrations

$\sqrt{\Delta H/c}$ versus w/c

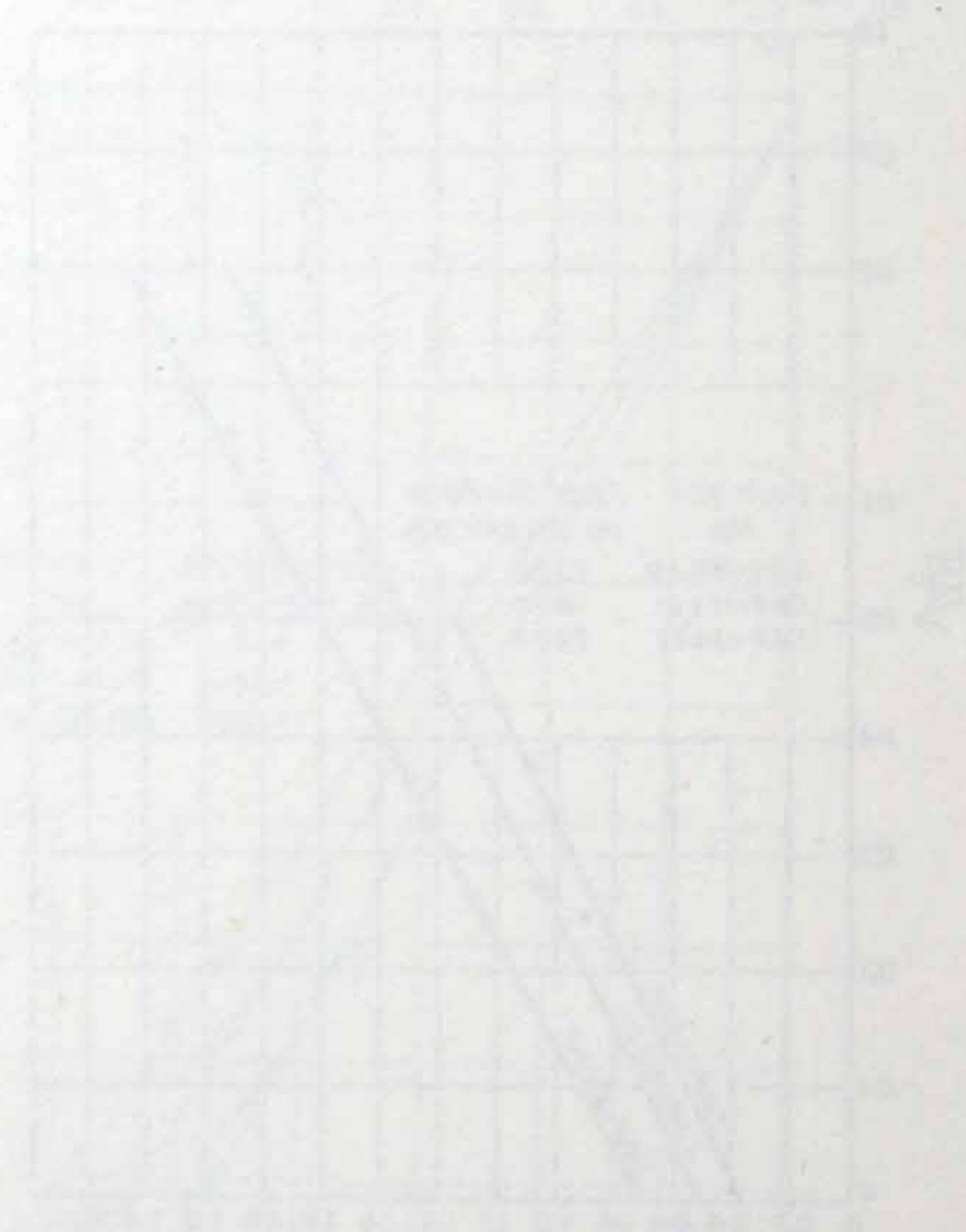
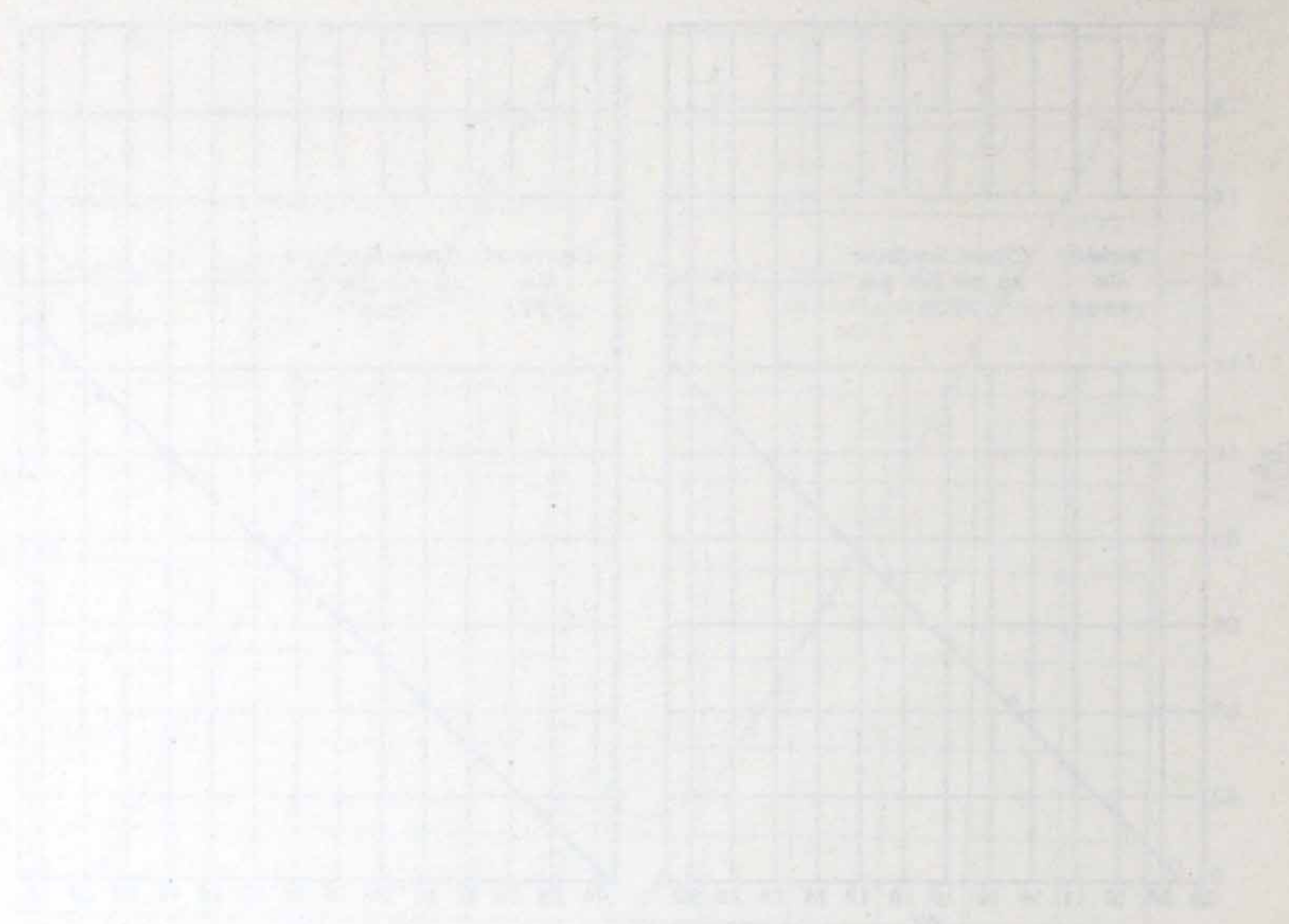


Fig. 2. A graph of the function $y = x$. The graph is a straight line passing through the origin (0, 0) and the point (10, 10). The x-axis and y-axis are labeled from 0 to 10.

For practical purposes of interpolation and moderate extrapolation linear representation of the data on a plot of $\sqrt{\Delta H'}/c$ versus w/c appears to be most generally satisfactory. Two well established points are needed to establish the line and more are preferable. However, for cements having specific surfaces from 1700 to 2000 sq cm per gm the slope is usually 0.50 ± 0.03 and for such cements a common value of 0.50 can be assumed if correction for only a small change in w/c is wanted and data are available for just one value of w/c .

The point where the straight line cuts the w/c -axis is the minimum value of w/c , at which the bleeding capacity apparently becomes zero. If this minimum value is represented by $(w/c)_m$ and the slope of the line by k , the equation of the line, as solved for $\Delta H'$, is

$$\Delta H' = k^2 c [w/c - (w/c)_m]^2 \quad (7)$$

The limit $(w/c)_m$ plays the same part in Equation 7 as the c_B in Equation 6 except that the two quantities represent different ways of defining the indicated limiting concentration; the additional significance that was attributed to c_B was wholly hypothetical. As long as the limiting, or base, composition is regarded only as the practical limit at which no bleeding occurs, no argument can be raised against the validity of the concept. However, the indicated limit will agree with the actual one only if the equation remains applicable at the highest concentrations. Equation 7 is believed to be sufficiently correct to give good relative values of the limiting w/c 's, values at which the actual bleeding capacities, if not zero, are at least very small. Table 3 gives the values of k and of $(w/c)_m$ that have been determined for cements of medium fineness. For effects of fineness see Fig. 6.

Implications of Empirical Relationships

Although the assumption of a linear relationship between $\sqrt{\Delta H'}/c$ and w/c for values of w/c below 3 appears

best for general purposes, the linearity of the relationship between $\sqrt{\Delta H'}$ and w (Fig. 5) is really very good for the coarser cements. Since for such cements the latter relationship is linear over the whole range in concentration, it may eventually prove useful as a guide to the basic principles that determine the bleeding capacity. Although empirical, it must at least be a close approximation to the general law governing the bleeding capacities of the cements in question. As shown in Appendix D, it indicates that the settled volume per unit of cement increases linearly with the initial water-content, w . It also indicates that the fraction of the excess* water in the initial paste that remains in the sediment is numerically the same as the fraction of the initial paste volume that can be regarded as constituting base volume. Perhaps this will be clearer if written as an equation, namely,

$$\frac{\text{excess water in sediment}}{\text{excess water in initial paste}} = \frac{\text{base volume}}{\text{initial paste volume}}. \quad (8)$$

The right-hand ratio of this proportion is a measure of the concentration and hence presumably of the stability of the initial floc-structure. The equation shows that this ratio gives, directly, the proportion of the excess water that will be retained by the cements that exhibit the linear relationship between $\sqrt{\Delta H'}$ and w .

In conclusion of this section, Fig. 7 is presented to show the different bleeding capacities likely to be found for cements of normal fineness in pastes of various water contents. Some discussion of the causes of the different values found for different cements will be given in subsequent sections.

*By excess water is meant the water in the initial paste in excess of that needed to form "base" volume with the amount of cement that is present. The base volume referred to here is, of course, that indicated by a plot like Fig. 5.

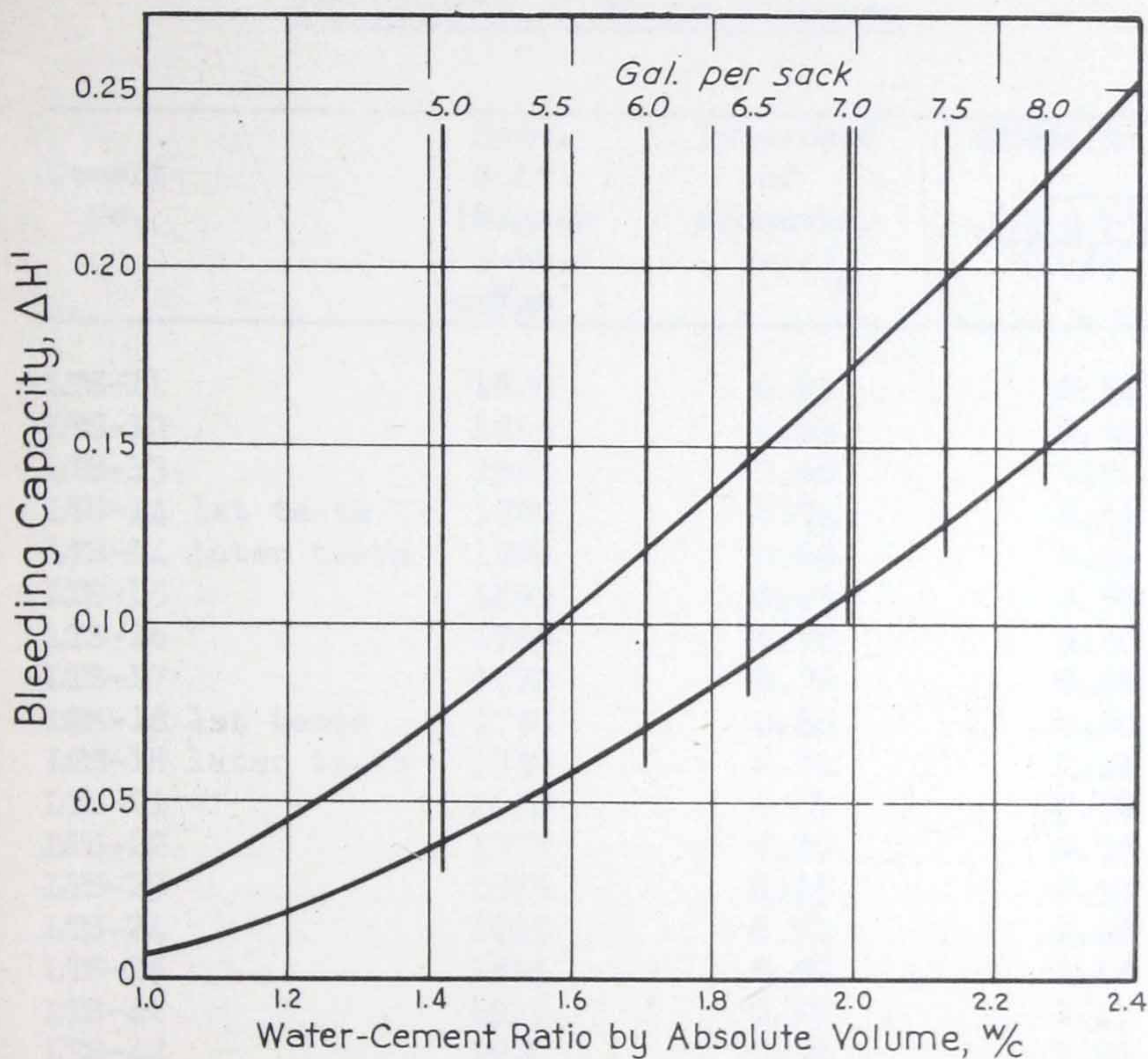


Fig. 7-Ranges in Bleeding Capacities

Most cements with specific surfaces of 1850 ± 100 sq. cm. per gm. will give pastes whose bleeding capacities fall within the band shown. The different amounts of bleeding found for different cements are attributable to differences in chemical constitution and in treatment as well as to differences in fineness.

Table 3

Data on $\sqrt{\Delta H'/c}$ versus w/c
for Cements of Medium Fineness

Cement No.	Spec. Surf. (Wagner Turb.) cm^2/gm	Intercept of w/c-axis, $(w/c)_m$	Slope k: $\frac{\Delta \sqrt{\Delta H'/c}}{\Delta w/c}$
LTS-11	1820	0.63	0.51
LTS-12	1815	0.63	0.50
LTS-13	1665	0.68	0.50
LTS-14 1st tests	1880	0.74	0.46
LTS-14 later tests	1880	0.66	0.49
LTS-15	1895	0.63	0.50
LTS-16	1785	0.58	0.50
LTS-17	1770	0.76	0.48
LTS-18 1st tests	1750	0.60	0.50
LTS-18 later tests	1750	0.72	0.49
LTS-21	1630	0.59	0.59
LTS-22	1775	0.80	0.53
LTS-23	1875	0.65	0.53
LTS-24	1925	0.71	0.48
LTS-25	1825	0.59	0.48
LTS-41	1915	0.67	0.45
LTS-42	1920	0.52	0.52
LTS-43	1965	0.76	0.47
LTS-43A	1915	0.55	0.38*
LTS-51	2025	0.55	0.45
SBR-15365	1665	0.64	0.52
SBR-15496	1740	0.73	0.53
SBR-15621	1820	0.50	0.49
SBR-15668	1830	0.52	0.52
SBR-15761	1800	0.65	0.53

*The cement which gave this unusually low value was ground from clinker that was not the normal plant product.

4. Relationship between Cement Fineness and the Bleeding Characteristics

Bleeding Rate

Equation 2 indicates that the bleeding rate is inversely proportional to the square of the specific surface of the cement if other quantities in the equation remain unchanged. However, the w_i term generally increases with the fineness of cements prepared from a given clinker, as was indicated in Bulletin 2 (p. 44). Data obtained since then are shown in Table 4. Of the 5 clinkers tested, one fails to show the relationship; but there is reason to believe that, for some of the cements prepared from that clinker, dehydration of gypsum during milling occurred and affected the bleeding characteristics. Presumably, if fineness were strictly the only independent variable, an increase in it would always mean an increase in w_i . However, as Table 4 shows, the degree of the effect is different for different clinkers. An intermediate case is illustrated by Fig. 8. This curve can be used to obtain a rough correction for w_i in other cases.

When bleeding rates have been accurately determined at a given water content for cements made from a given clinker but ground to different finenesses, a plot of

$Q^{1/3}$ versus $\frac{1}{\text{sp. surface}}$ can be used for purposes of in-

terpolation. The relationship has been found to be fairly linear, especially for difference in fineness of only 300 or 400 sq cm per gm. For SBR clinker No. 1 the three finenesses of 1040, 1665, and 2280 sq cm per gm give an almost exactly straight line.

Changes in bleeding rate caused by changes in fineness, and also ones caused by changes in water content, can be estimated directly from a plot like Fig. 24 of Bulletin 2, which has been reproduced here as Fig. 9

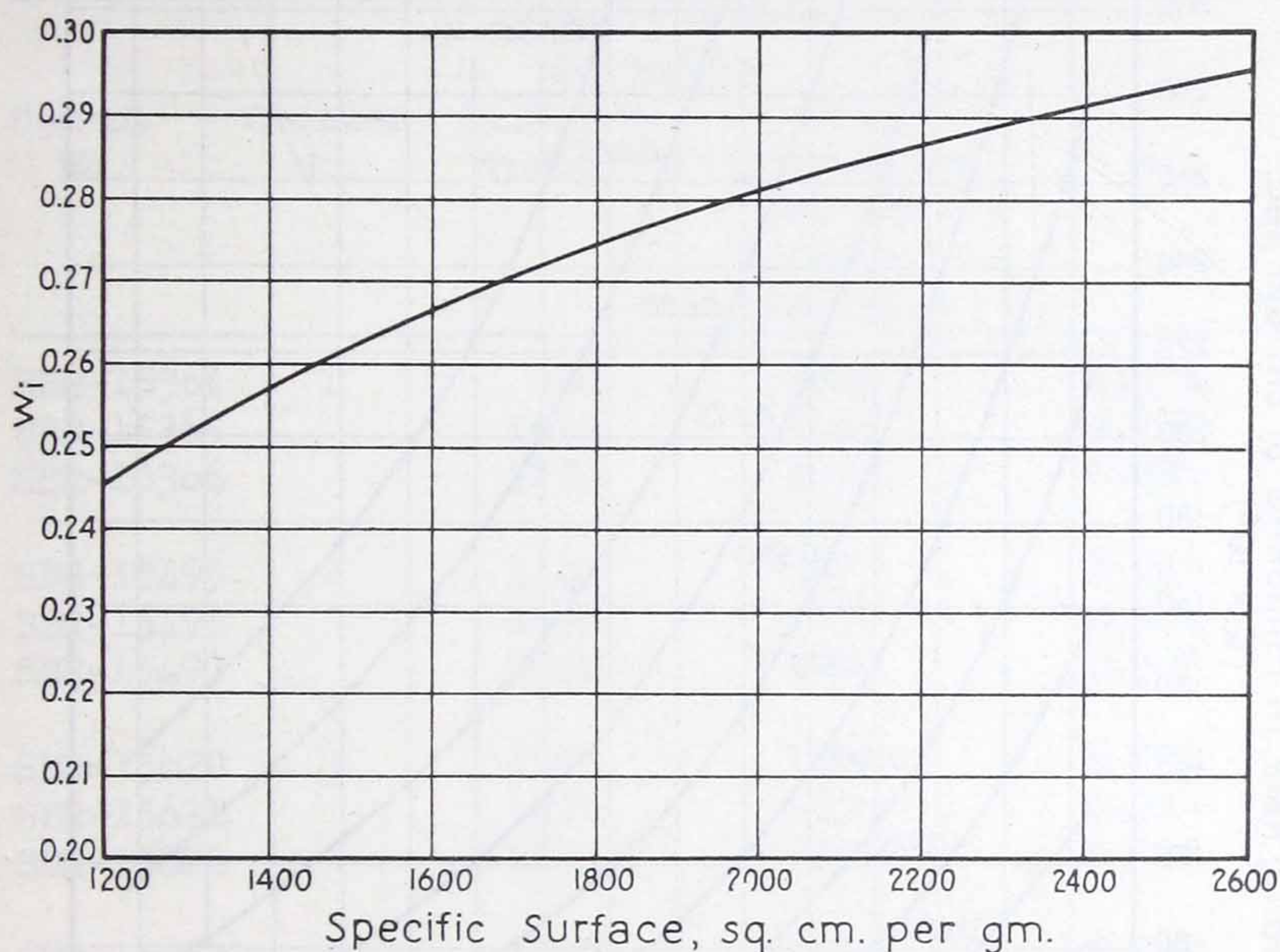


Fig. 8 — The Change in w_i with Change in Specific Surface as Indicated by Data for Cements from Clinker No.1

This plot can be used to estimate the effect of fineness on the w_i values of other cements if the changes in fineness are small.

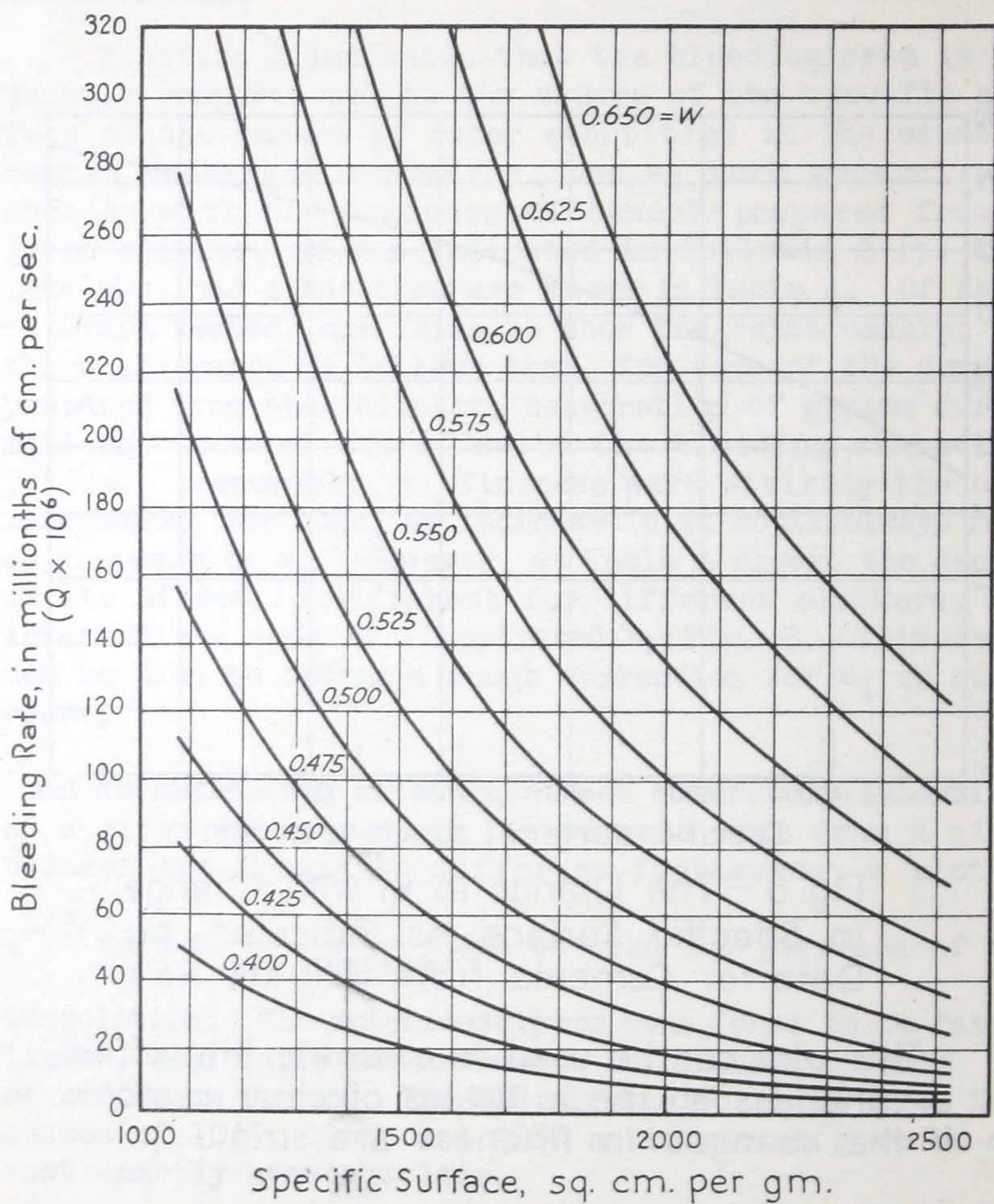


Fig.9 - Effects of Fineness of Cement and of Water Content of Paste on Bleeding Rate, as Indicated by Data for a Particular Set of Cements

Table 4

Effect of Specific Surface on the Magnitude of w_1

Cement No.	Clinker No.	Specific Surface, sq cm/gm		w_1
		(A.S.T.M. Turb.)	With Correction for +60 micron Particles	
SBR-15364	1	980	1040	0.234
SBR-15365		1640	1665	0.269
SBR-15366		2270	2280	0.296
SBR-15495	2	1440	1470	0.249
SBR-15496		1695	1740	0.274
SBR-15497		2500	2500	0.320
SBR-15620	3	1200	1375	0.232
SBR-15621		1825	1820	0.249
SBR-15622		2290	2200	0.266
SBR-15667	4	1200	1250	0.249
SBR-15762		1475	1500	0.229
SBR-15763		1800	1800	0.226
SBR-15669		2290	2290	0.249
SBR-15696	5	1260	1305	0.248
SBR-15760		1465	1500	0.264
SBR-15761		1780	1800	0.285
SBR-15698		2255	2265	0.292

(with a change in the bottom scale to units of sq cm per gm). Though such a plot is strictly applicable only to the cements from the one particular clinker on which it is based, it can be used to obtain approximate estimates for other cements when their bleeding rates are known for one fineness and water content. When the bleeding rate for another fineness is sought, the first step is to locate the point corresponding to the known bleeding rate and the fineness at which it was obtained. Then, regardless of whether the water-content indicated by the plot is the same as was used in the test, it is treated as if it were, and thus the point corresponding to the new fineness is found. The bleeding rate indicated by this point is approximately that which would be obtained experimentally at the new fineness. If the effect of a change in water content is sought, the procedure consists first in locating the point corresponding to the experimental bleeding rate and the water-content at which it was obtained, then in following along the vertical (constant specific surface) line through the initial point until the point corresponding to the new water content is reached. The bleeding rate indicated by this point is the estimated value for the new water content. These methods are simply convenient means of obtaining approximate estimates, but they usually check with experiment rather well.

Bleeding Capacity

The effect of cement fineness on the bleeding capacity is shown by the data of Table 5. These data indicate that the decrease in bleeding capacity for an increase of 100 sq cm per gm in the specific surface of the cement is usually 0.011 ± 0.004 within the practical range of concentrations. The data vary for the different groups of cements; when more than a small change in fineness is involved, the resultant bleeding capacity had best be determined by direct test if an accurate value is wanted.

Table 5

Effect of Cement Fineness on Bleeding
Capacity, $\Delta H'$

Cement No.	Clink- er No.	Sp.Surf. cm ² /gm (Turb.)	At w/c = 1.6		At w/c = 1.8		At w/c = 2.0	
			Bleeding Capacity, $\Delta H'$	Change in $\Delta H'$ per 100 cm ² /gm	Bleeding Capacity, $\Delta H'$	Change in $\Delta H'$ per 100 cm ² /gm	Bleeding Capacity, $\Delta H'$	Change in $\Delta H'$ per 100 cm ² /gm
SBR-15364	1	1040	0.174	0.0130	0.219	0.0138	0.256	0.0139
SBR-15365		1665	0.093	0.0107	0.133	0.0133	0.169	0.0146
SBR-15366		2280	0.027		0.051		0.079	
SBR-15495	2	1470	0.119	0.0157	0.172	0.0215	0.206	0.0222
SBR-15496		1740	0.074	0.0079	0.114	0.0113	0.146	0.0139
SBR-15497		2500	0.014		0.028		0.041	
SBR-15620	3	1375	0.154	0.0108	0.202	0.0117	0.237	0.0117
SBR-15621		1820	0.106	0.0137	0.150	0.0153	0.185	0.0163
SBR-15622		2200	0.054		0.091		0.123	
SBR-15667	4	1250	0.167	0.0080	0.214	0.0080	0.249	0.0084
SBR-15762		1500	0.147	0.0070	0.194	0.0077	0.228	0.0071
SBR-15763		1800	0.126	0.0088	0.171	0.0096	0.206	0.0102
SBR-15669		2290	0.083		0.124		0.156	
SBR-15696	5	1305	0.145	0.0097	0.192	0.0108	0.225	0.0103
SBR-15760		1500	0.126	0.0106	0.171	0.0113	0.205	0.0117
SBR-15761		1800	0.094	0.0071	0.137	0.0080	0.170	0.0086
SBR-15698		2265	0.061		0.100		0.130	
Average change in $\Delta H'$ per 100 cm ² /gm (omitting SBR-15495):				0.010		0.011		0.0115

5. Relationships between Bleeding Rates and Bleeding Capacities

The Experimental Evidence

A comparison of Figs. 2 and 7 shows that bleeding rate and bleeding capacity increase in similar manner when the water-cement ratio is increased. Indeed, for a given cement, the bleeding rates are almost proportional to the bleeding capacities, at least for bleeding rates up to 300×10^{-6} cm per sec. However, the straight line that best represents the data on a plot of bleeding rate, Q , versus bleeding capacity, $\Delta H'$, commonly cuts the Q -axis at a small positive value, generally less than 30×10^{-6} cm per sec. (See Fig. 10) At values of Q above $300-350 \times 10^{-6}$ cm per sec the data-points tend to fall above the straight line that represents the lower values.

The relationship between bleeding rate and bleeding capacity sometimes remains quantitatively unchanged as the fineness to which a cement is ground is changed markedly. This is most common within the range of moderate to high finenesses; a cement coarser than 1500 sq cm per gm is likely to show a higher bleeding rate for a given bleeding capacity. Fig. 10 shows the relationships between bleeding rate and bleeding capacity for cements from five clinkers. For only one clinker does the slope of the data-line decrease significantly with each increase in fineness throughout the whole range from coarse to very fine. This is for clinker No. 5 which is the only one that is high in alkali (total alkali oxides = 1.57%). That this alkali is probably partly responsible for the decreases in slope is indicated by data to be discussed in the next paragraph; the rate at which the alkali goes into solution increases, of course, with the fineness of the cement.

It is apparent from Fig. 10 that the relationship between bleeding rate and bleeding capacity differs somewhat for cements of the same fineness that are made from

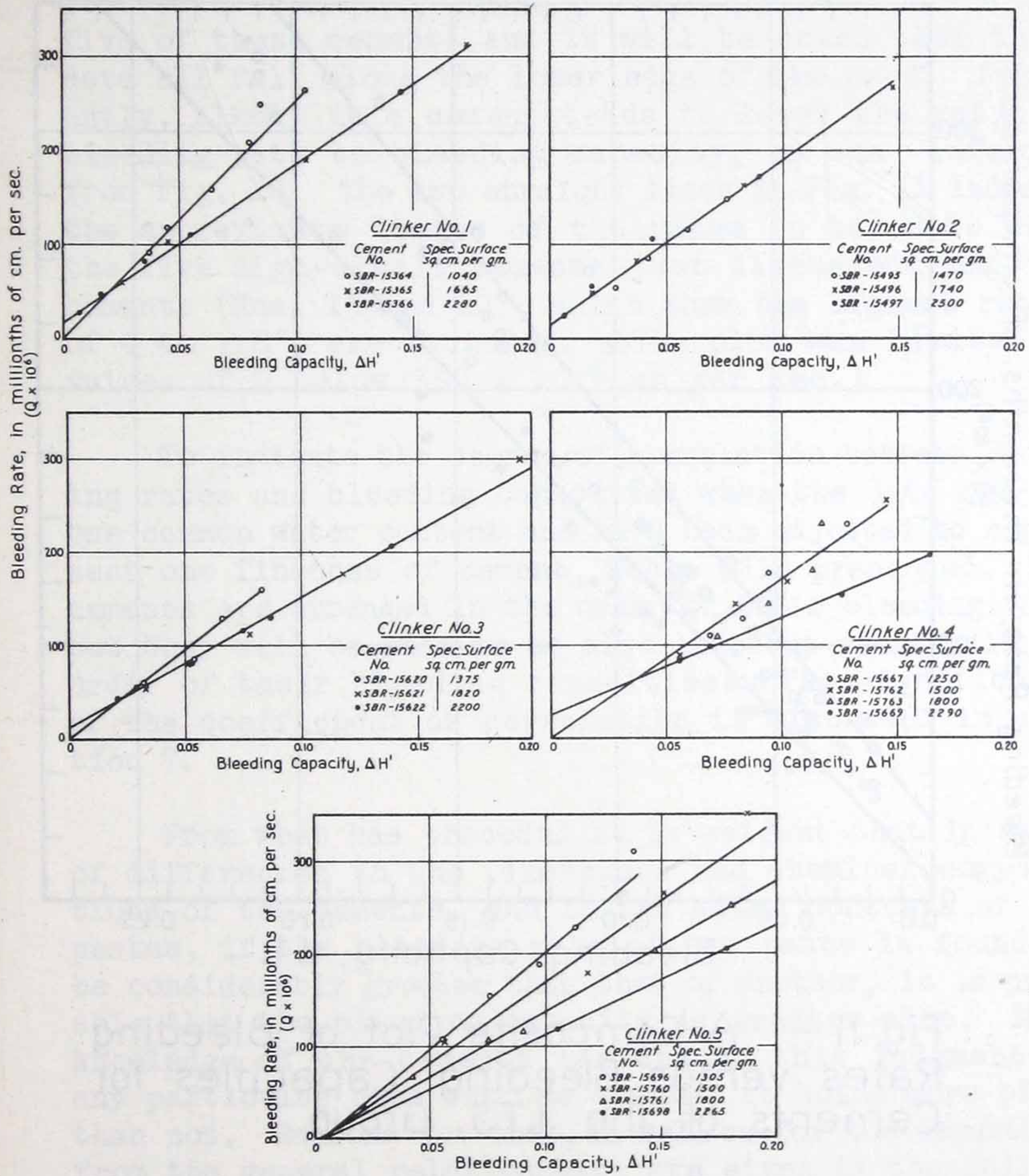


Fig. 10 - Relationships Between Bleeding Rates and Bleeding Capacities

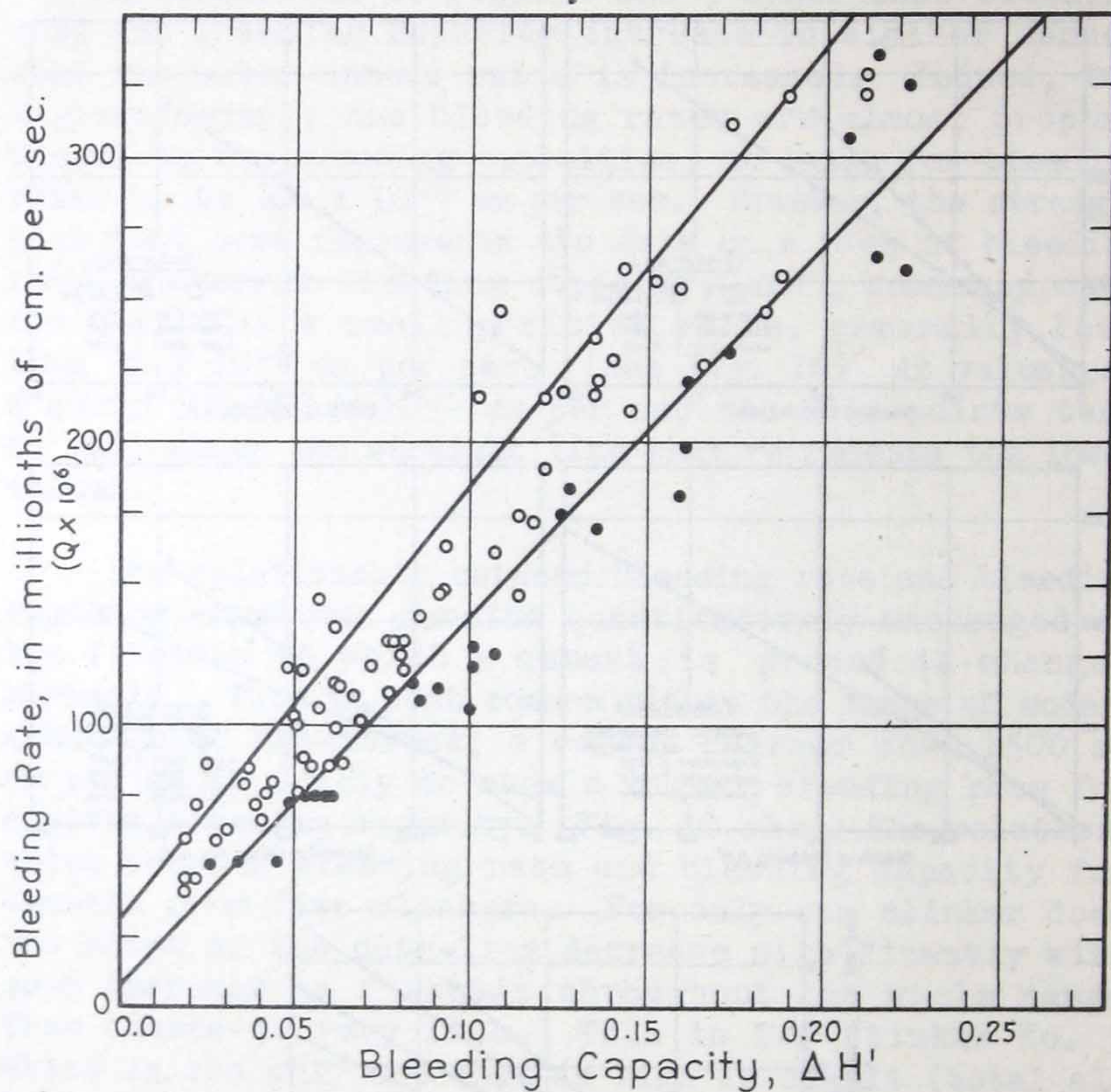


Fig. II — A Composite Plot of Bleeding Rates versus Bleeding Capacities for Cements of the LTS Group

different clinkers. In Fig. 11 the data for the cements of the LTS group that are not high-early-strength or air-entraining cements have been placed on one plot to show the degree of spreading. Data for the cements that showed free alkali in excess of 6.8 by the Merriman test have been represented by solid circles. There were five of these cements and it will be noted that their data all fall along the lower edge of the band. Apparently, alkali in a cement tends to lower the ratio of bleeding rate to bleeding capacity, as was inferred from Fig. 10. The two straight lines in Fig. 11 indicate the approximate limits of the range in the data when the five high-alkali cements just discussed, and two cements (Nos. 13 and 22), which show the highest ratios of Q to $\Delta H'$, are excluded. (The plot was limited to values of Q below 350×10^{-6} cm per sec.)

To indicate the degree of correlation between bleeding rates and bleeding capacities when the data are for one common water content and have been adjusted to represent one fineness of cement, Table 6 is presented. The cements are arranged in the order of their bleeding rates but they will be seen to be also lined up roughly in the order of their bleeding capacities. The significance of the coefficient of correlation is discussed in section 7.

From what has preceded it is evident that in spite of differences in the finenesses and chemical compositions of the cements, and in the water contents of the pastes, if the bleeding rate of one paste is found to be considerably greater than that of another, it is probable that the bleeding capacity is greater also. More knowledge of the cements can change this judgment in any particular case but, as a rule, it holds more often than not. Reasons for this, as well as for the departures from the general relationship, are given in the following discussion.

Table 6

Bleeding Rates and Bleeding Capacities as
Adjusted to Correspond to a Specific Surface
(Turb.) of 1840 sq cm per gm

From tests at 23.5°C using a water-
 cement ratio of 0.466 by weight.

Cement No.	Bleeding Rate, Q, cm per sec, x 10 ⁶	Bleeding Capacity, ΔH'
LTS-42	163	0.123
LTS-23	156	0.096
LTS-51	144	0.097
LTS-15	140	0.084
LTS-21	140	0.099
LTS-16	129	0.097
LTS-11	117	0.078
LTS-12	116	0.081
LTS-18	115	0.068
LTS-22	111	0.046
LTS-25	107	0.084
LTS-13	104	0.048
LTS-43A	98	0.061
LTS-43	88	0.067
LTS-41	85	0.069
LTS-24	80	0.062
LTS-14	79	0.054
LTS-17	78	0.050

Coefficient of correlation between
 bleeding rate and bleeding capacity: 0.84
 Odds against chance correlation: 12,300 to 1

Theoretical Considerations

That both bleeding rate and bleeding capacity should increase as the dilution of a paste is increased is easy to understand and needs no elaboration. It can also be readily seen that an increase in fineness should reduce the bleeding rate since it reduces the sizes of the capillary spaces through which the liquid flows between particles. That bleeding capacity should also be reduced is not so immediately evident. Indeed, a given volume of inert particles of a given shape and a given relative grading would give a constant gross volume of sediment, irrespective of fineness, if a given arrangement of particles were maintained. The fact that the bleeding capacity for a given water-content does ordinarily decrease with fineness can be attributed to the flocculated state of the paste and to the fact that a little chemical reaction evidently occurs during mixing. With a constant flocculating force per unit of surface, the greater ratio of surface to particle-weight in a finely ground powder should cause the powder to stop settling before it had developed as compact an arrangement as would be reached by a coarser powder. This could account for the whole of the observed effect, but probably chemical reaction plays a part also. As already stated, a coating of hydrate is believed to be formed on the cement particles when they first contact the water. Hence, for a given thickness of layer the total solid volume is greater the finer the cement, and can have more of an effect on the bulk of sediment.

Differences in the chemical reactivities of different cements may be expected to affect bleeding rate and bleeding capacity somewhat similarly if they are manifested principally through different thicknesses of reaction layers on the cement particles. The relative thicknesses of the layers would determine the relative spaces between particles, and hence the relative bleeding rates. They would determine the relative effective diameters of the particles and hence also the relative volumes of sediment, provided the arrangements of the

particles were the same. This effect on the volumes of sediment would, presumably, be too small to account for all the observed differences, but loosely formed hydrate layers of different thicknesses would be expected to produce differences in the structures of the settled pastes. Such layers could deform at points of contact as the particles came to rest, and they could thus broaden and strengthen the contacts. Thicker layers would broaden the contacts more effectively than thinner layers and could thus stabilize less compact structures.

The speculative and merely qualitative elements in the matters discussed constitute one reason why caution is needed in estimating bleeding capacities from bleeding rates. A more positive reason to expect departures from good correlation arises from the possibility that there may be material differences in the strengths of the flocculating forces developed by different cements. When the flocculating forces are strong enough to maintain the floc structure intact, an increase in the strength of the flocculating agent has little effect on the bleeding rate; this is shown by the tests on silica powder that were reported in Bulletin 2. The same tests show, however, that the bleeding capacity is strongly affected by the strength of the flocculating agent. Hence, if two cements are otherwise the same but develop flocculating forces of materially different strengths they may show the same initial bleeding rates but distinctly different bleeding capacities. The fact that there is as much correlation between bleeding rates and bleeding capacities as is found when different cements are involved seems to indicate that usually the strengths of the flocculating forces are not widely different for different cements. Possible differences in flocculation will be considered again when the effects of alkali hydroxides are discussed.

6. Duration of Bleeding

For heights of paste-sample for which bleeding is completed before the end of the so-called dormant period, the duration of bleeding is often strikingly insensitive to change in the water content of the paste and in the fineness of the cement. Bleeding times for a constant height of sample (3.3 cm) are given in Table 7. Many of these data show the constancy just mentioned. However, for the very finely ground cements the bleeding time increases with the water-content of the paste.

In Table 7, the figures for $\frac{3.3 \Delta H'}{60Q}$ are the times, in minutes, in which bleeding would have been completed had the settlements continued at the initial rates. The ratios of the actual bleeding times to these "minimum" times are given in the columns headed R. Though apparently not closely reproducible, these ratios are, in all cases, practically independent of the water-contents of the pastes. They average about 1.5 for most of the cements but are significantly higher in a few instances. Since R is so independent of water-content, maintenance of a practically constant bleeding time when the water-content is changed usually means that the ratio of $\Delta H'$ to Q has stayed fairly constant.

For pastes that complete their settlement within the dormant period the bleeding time is approximately proportional to height of sample. Though this relationship is only approximate (Bulletin 2, p. 8), it seems to hold fairly well in most cases, when wall effects are avoided. Fig. 12A shows the curve for a cement that had an estimated dormant period of 60 minutes. Tests, in the same vessel, on cements with longer dormant periods have usually shown considerable departure from the straight line before the end of the estimated dormant period (see Fig. 12B), but this may be because the heights of the samples considerably exceeded the diameter of the vessel (see Bulletin 2, p. 141). When bleeding time is proportional to paste height, the ratio (R) of the total bleeding time to the time based on the

Table 7

Bleeding Times and Other Data
for Cement Pastes 3.3 cm in Height*

R = Ratio of bleeding time to $\frac{3.3 \Delta H'}{60Q}$

Clink- er Ref. No.	Coarse				Cement Medium				Very Fine			
	w	SBR-15364 Time, $\frac{3.3 \Delta H'}{60Q}$ min.		R	w	SBR-15365 Time, $\frac{3.3 \Delta H'}{60Q}$ min.		R	w	SBR-15366 Time, $\frac{3.3 \Delta H'}{60Q}$ min.		R
1	0.457	34	22	1.55	0.518	31	23	1.35	0.520	20	14	1.4
	0.478	28	21	1.3	0.568	33	24	1.4	0.570	26	19	1.35
	0.498	33	22	1.5	0.618	46	30	1.5	0.620	29	23	1.25
	0.517	32	21	1.5	0.670	43	30	1.4	0.650	39	27	1.45
	0.517	28	19	1.45					0.720	39	30	1.3
	0.543	32	22	1.45								
SBR-15495					SBR-15496				SBR-15497			
2	0.490	39	28	1.4	0.516	33	20	1.65	0.568	20	14	1.45
	0.514	44	27	1.65	0.566	37	24	1.55	0.618	25	18	1.4
	0.539	39	28	1.4	0.617	45	28	1.6	0.668	31	23	1.35
	0.564	42	28	1.5	0.665	44	30	1.45	0.718	38	29	1.3
SBR-15620					SBR-15621				SBR-15622			
3	0.470	50	29	1.7	0.501	52	34	1.55	0.542	44	27	1.65
	0.495	55	34	1.6	0.542	48	34	1.4	0.562	45	29	1.55
	0.520	48	28	1.7	0.581	50	38	1.3	0.601	56	36	1.55
	0.545	53	29	1.85	0.622	52	37	1.4	0.628	55	36	1.55
					0.671	50	36	1.4	0.649	55	37	1.5
									0.702	52	32	1.6
SBR-15762					SBR-15763							
4	0.510	50	35	1.45	0.550	57	36	1.6				
	0.540	60	31	1.95	0.575	64	36	1.8				
	0.560	60	33	1.8	0.600	60	35	1.7				
	0.600	60	31	1.95	0.625	60	28	2.15				
SBR-15760					SBR-15761				SBR-15698			
5	0.550	52	30	1.75	0.550	58	34	1.7	0.550	50	33	1.5
	0.600	53	36	1.45	0.600	58	39	1.5	0.650	68	49	1.4
	0.625	52	31	1.7	0.600	60	43	1.4	0.700	75	48	1.55
	0.650	51	29	1.75	0.650	60	40	1.5				

*The actual paste heights were not all 3.3 cm, but the bleeding times were adjusted by assuming bleeding time to be proportional to paste height.

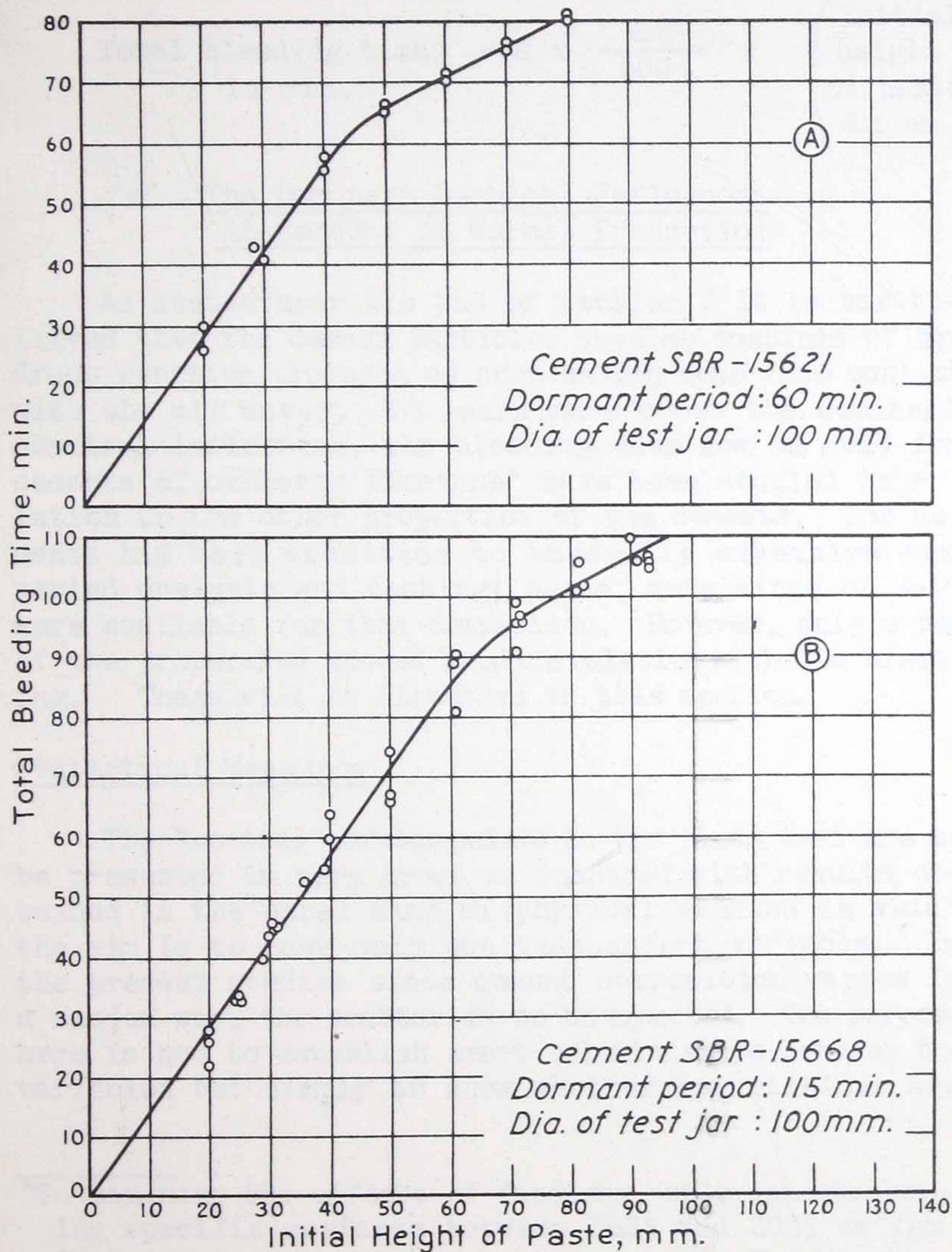


Fig. 12 - Bleeding Time versus Height of Paste-Sample

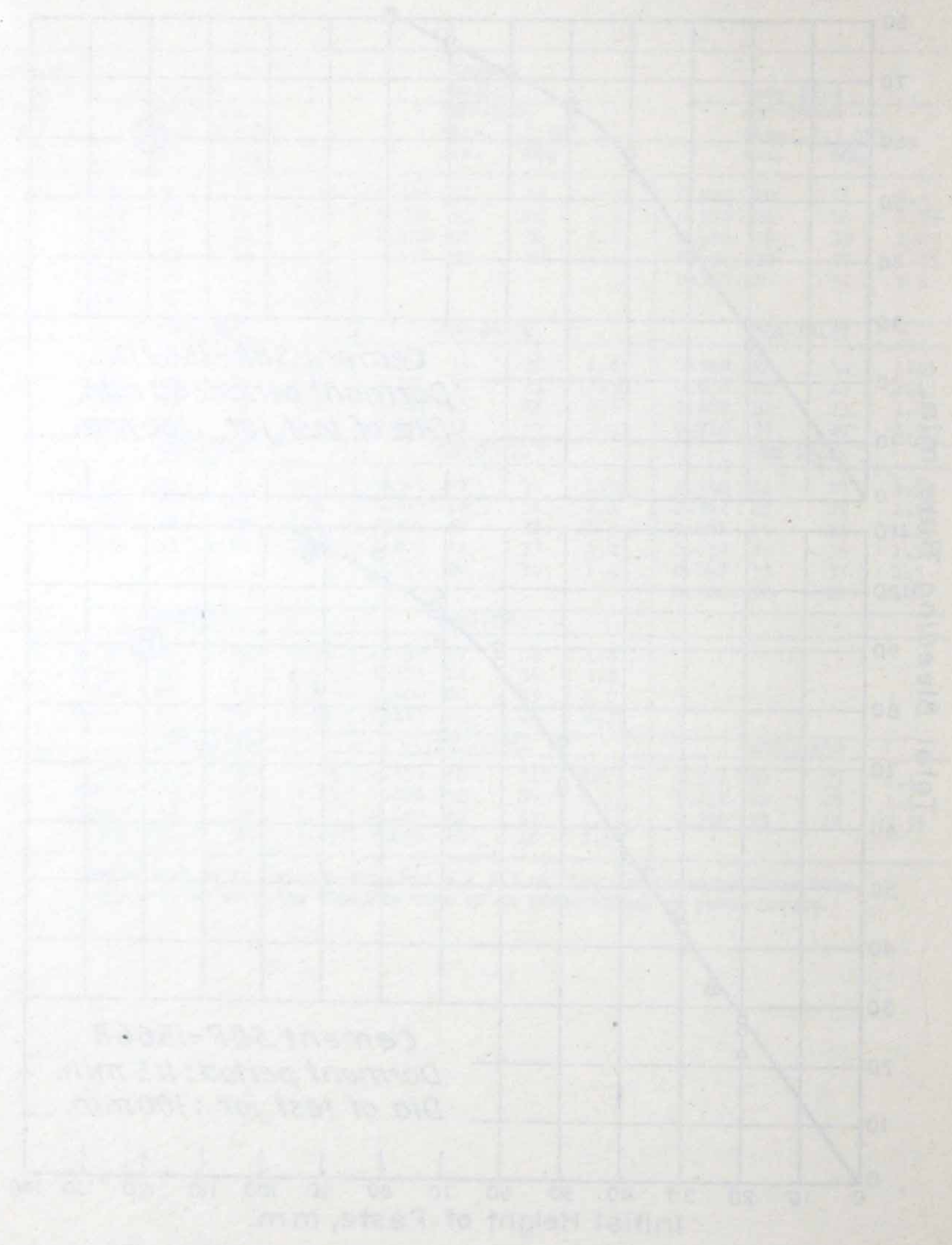


Fig. 12 - Bleeding Time versus Height of Paste Samples

initial rate is about the same for different heights. This may be seen from the following equation, since both Q and $\Delta H'$ are practically independent of paste height under proper test conditions.

$$\text{Total bleeding time, in min.} = R \times \frac{\Delta H'}{60Q} \times \left(\begin{array}{c} \text{Initial} \\ \text{height} \\ \text{of paste} \\ \text{in cm} \end{array} \right)$$

7. The Dominant Chemical Influences in Cements of Normal Production

As stated near the end of section 2 it is now believed that the cement particles develop coatings of hydrous reaction products as soon as they come into contact with the mix water. To learn more about the dominant chemical influences, the bleeding data now on hand for cements of ordinary fineness* have been studied in relation to the other properties of the cements. The cements had been submitted to unusually extensive and varied analysis and testing; hence, many kinds of data were available for this comparison. However, only a few of the properties showed good correlation with the bleeding. These will be discussed in this section.

Statistical Measures

The "scatter" of the points in the plots that are to be presented is very great as compared with results obtained in the usual kind of physical studies in which the aim is to have only one independent variable. In the present studies since cement composition varies in a random way, the scatter is to be expected. The purpose here is not to establish exact relationships between the variables but simply to show whether correlations are

*To minimize the effects of fineness, only cements having specific surfaces between 1625 and 2025 cm^2/gm (A.S.T.M.) were utilized in this study. The bleeding data were used both as determined and after adjustment to correspond to 1840 cm^2/gm .

indicated and how good the indications are. To this end, coefficients of correlation, and the odds against the correlations' being purely fortuitous, have been calculated and have been recorded on the plots.

The coefficients are the Pearson coefficients of correlation (12) which are widely used by statisticians. They may be defined for present purposes simply as index numbers which indicate the degree to which a linear relationship can be assumed between two variables. The value is zero when there is no correlation, and is +1 when the points all fall on one straight line. A negative sign indicates that as the one variable increases the other decreases. It is not easy to state the exact significance of any particular value between 0 and 1, though of course the greater the absolute magnitude the greater is the indicated correlation.* The present interest, however, lies not so much in the degree of correlation which the data indicate but in the judgment which this makes possible as to whether the two properties being studies are really dependent on each other.

*However, the coefficient, or rather 100 times it, may be said to represent approximately the percentage of "overlapping" between the deviations of the two variables from their averages. That is, if the coefficient is 0.60, and the conditions are symmetrical with respect to the two variables, 60% of the difference of one variable from its mean is determined, on the average, by 60% of the difference of the other variable from its mean, and vice versa, there being thus 40% of each departure from the mean that is determined by factors that are independent of the value of the other variable (12). For example, if the two variables that are being compared are A and B, but there are other variables C, D, E, etc., then if C influences A but not B, C is one of the factors determining the 40% of the variation in A that is not attributable to B. Likewise, D might affect B but not A.

That is, though a calculated coefficient of correlation represents the particular data on which it is based, it is only an approximation to the value that would be obtained if an infinite number of pairs of data were available. The latter value can be considered to give the true correlation between the two properties that are being compared. Hence, the question of most immediate concern is this: Having obtained experimentally a given value of the coefficient of correlation what are the chances that an infinite number of tests would also show correlation of the same kind, though perhaps different in degree? Since the infinite number of tests is not available, such a question may appear to be impossible of solution. However, since only chances, or odds, are under consideration, a solution can be obtained on the basis of the theory of probability. As might be expected, the result depends not only upon the size of the coefficient that is found experimentally, but also upon the number of pairs of data on which the coefficient is based, for, obviously, any particular value found for the coefficient is more likely to denote a true relationship if the number of tests is large than if it is small. It is not advisable here to go fully into the method of estimating the odds, as it can be found in standard texts.*

*The method of calculating odds that was used for this report was based on the "normal" probability curve. The ratio of the coefficient of correlation to the "standard error for zero correlation" (which latter is simply $1/\sqrt{N-1}$, where N is the number of pairs of tests) was used as entry to a table of the probability integral. By this means the numerical probabilities were obtained, both for and against the assumption that the correlation was fortuitous. The ratio of these probabilities gives the odds. Details and further explanation are given in reference (12). There is a more precise method (12) based on the work of Student, but since it gives greater odds the results reported here are at least on the conservative side. Some authors (12) report the odds against obtaining

However, the odds may at least be defined more precisely than was done on the plots. They are the odds against obtaining purely by chance a coefficient of correlation as large as that found experimentally. That is, if there is in fact no true correlation, these are the odds against obtaining by chance a coefficient at least as large numerically (i.e., either + or -) as was found.

Since the purpose in figuring the odds is to enable one to form a judgment as to whether there is true correlation, it is worth noting that, in statistical studies, odds of less than 20 to 1 (calculated as for this report) are often disregarded. On the other hand, odds of around 400 to 1 are usually considered highly significant. Odds of 20 to 1 correspond to a probability against correlation that amounts to about 5% of certainty, whereas the corresponding probability for odds of 400 to 1 is only 0.25%.

With these facts in mind, attention can be turned to the experimental data. For simplicity, all plots have been based on the same sets of data for bleeding rate and bleeding capacity, respectively, except for Figure 17, which is introduced to show that other sets of data sometimes give better correlation. In all the other plots the bleeding data correspond to a water-cement ratio of 0.466 by weight and a temperature of 23.5°C (74°F). The data have been adjusted to correspond in each case to a specific surface of 1840 sq cm per gm.

Perhaps the odds shown on the diagrams differ more widely than would seem to be justified by the difference in appearance of the plots. The odds, however, are in

by chance a correlation having the same sign (+ or -) as is indicated by the data. Such odds are about twice as great as those calculated for this report, which are based only on the absolute value of the coefficient. Hence, here again the method that was used gave conservative results.

no sense a linear measure of the "scatter". The coefficient of correlation is more nearly, though not strictly, of that nature. The fact that the odds increase so rapidly for a small improvement in correlation is not something that can be "seen" in the plots, but is simply an outcome of probability theory--which has as one of its purposes the avoidance of errors of purely intuitive judgment.

As a matter of fact, no great significance should be attributed to the exact odds when they are very high, for the method of calculation is approximate only. The main point to observe is simply whether or not the odds are considerably greater than a value which one is willing to accept as probably indicating true correlation.

Heat Liberation

A relationship between bleeding capacities and rates of heat liberation, both determined at 90°F, was noted first by W. C. Hansen. Study of other sets of heat data, both rates of heat liberation and cumulative heats for periods of 1 hour or less, has shown in many cases rather good correlation with both bleeding rate and bleeding capacity. Two of the better correlations are illustrated by Figs. 13A and 13B, which show the rates of heat liberation after 1 hour at 75°F plotted against bleeding rate and bleeding capacity, respectively. Figs. 14A and 14B are based on the amounts of heat liberated during the first 5 minutes at 75°F.

The sizes of the coefficients and the odds against chance correlation indicate that the rate and amount of bleeding are dependent to a considerable degree on something that is a prominent source of heat during the early history of the paste. Heats of solution contribute significantly to the heat liberated during the first few minutes, but the good correlation between the bleeding and the heat liberation at one hour makes it highly probable that chemical reaction is responsible for all the various correlations with the heat data. Reactions of

tricalcium aluminate appear most probable in this connection because of the relatively great reactivity of the C_3A and because, in reacting, C_3A liberates more heat per gram than any other cement compound except free lime. Only reaction which occurs during the mixing period can affect the initial bleeding rate; the correlation with the later heat liberation indicates simply that the same reaction is continuing. That the further reaction leaves the initial bleeding rate unaffected for a considerable period is evidently due in large measure to the fact that the reaction rate quickly falls to a small value. (See Fig. 1* and also the discussion in section 2.)

Readily Leached SO_3

Another property which was found to correlate rather well with the bleeding is the amount of SO_3 that can be leached from the cement in a short time. The concentrations of SO_3 obtained by Hansen and Pressler (8)** in five extractions of each cement were added together to obtain the values plotted in Fig. 15. The odds against

*The total heat liberated during the first 5 minutes is usually 3 or 4 calories per gram of cement, whereas that liberated during the next half hour is less than a calorie. Heat of solution during the 5-minute period is apparently only a few tenths of a calorie, except for the effect of free lime. Free lime can increase the heat of solution materially, but in general the initial heat liberation is judged to be sufficiently greater than is to be expected from heat of solution to justify the assumptions made regarding chemical reaction.

**A change in the method of extraction placed the data for 5 of the cements on a basis somewhat different from the rest. However, one cement was tested by both methods and the concentrations checked closely.

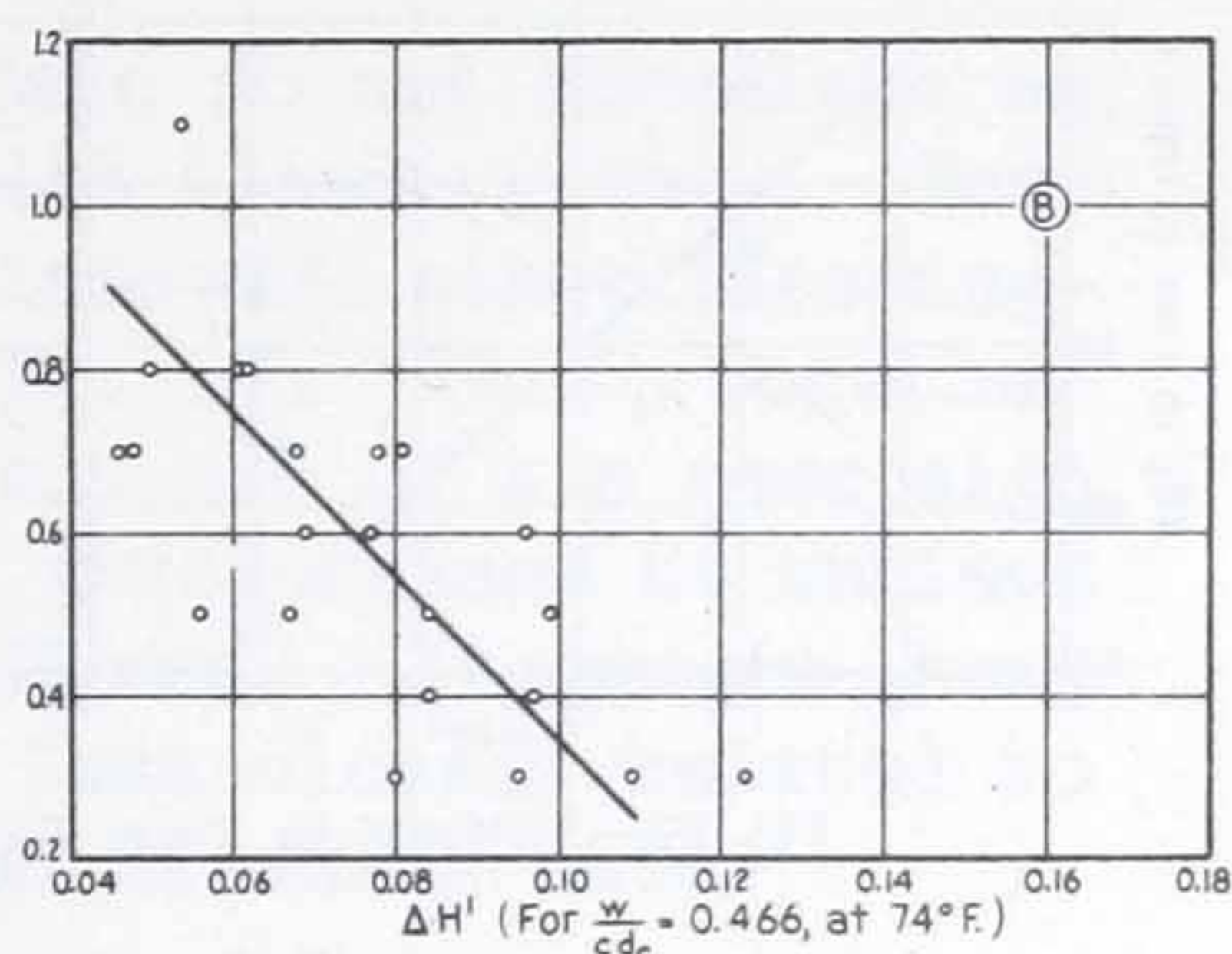
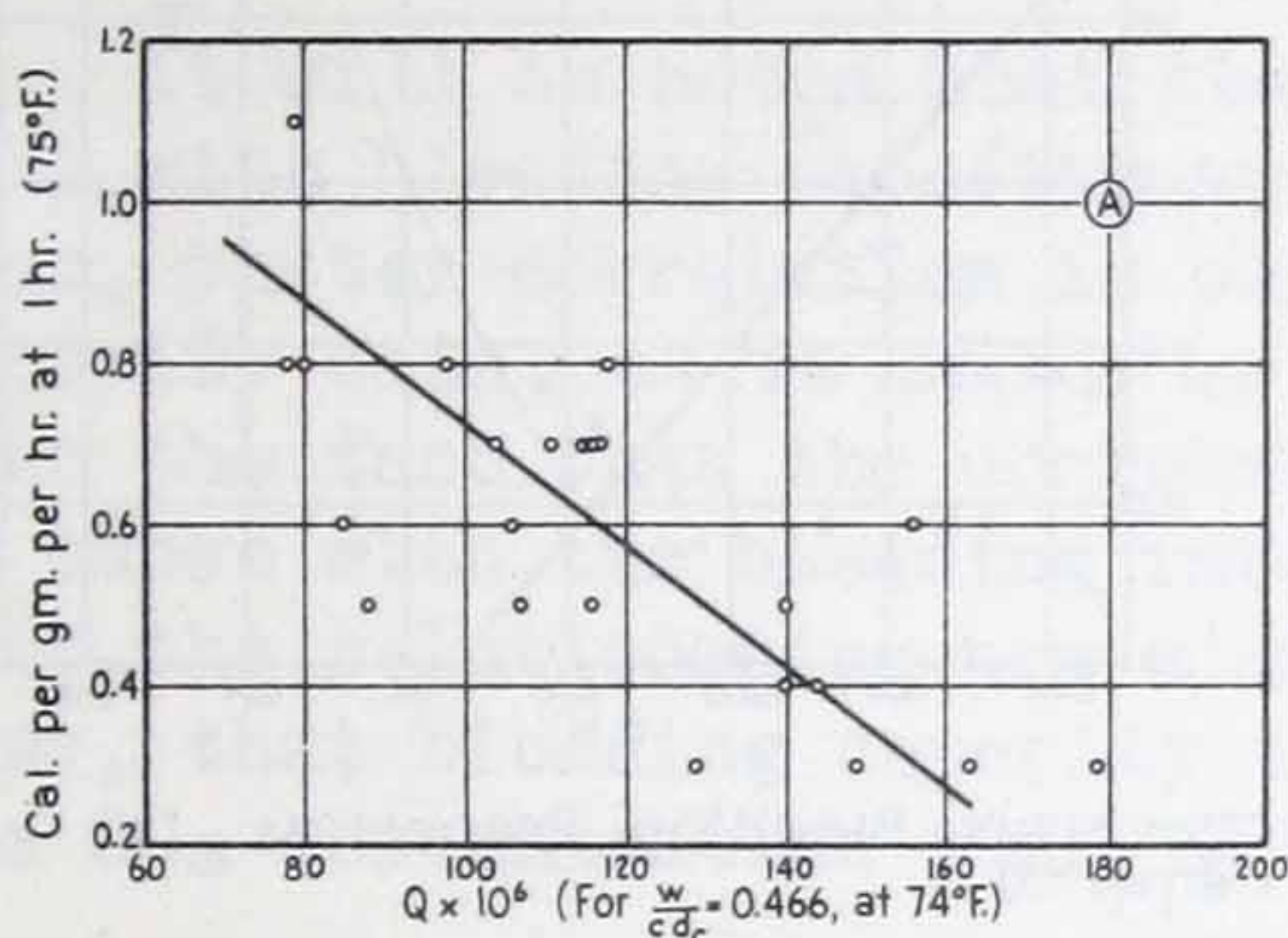


Fig. 13 - Rate of Heat Liberation versus Bleeding Properties
(23 Cements)

- Ⓐ Correlation with bleeding rate
Coefficient of correlation: -0.74
Odds against chance correlation: 2070 to 1
- Ⓑ Correlation with bleeding capacity
Coefficient of correlation: -0.72
Odds against chance correlation: 1380 to 1

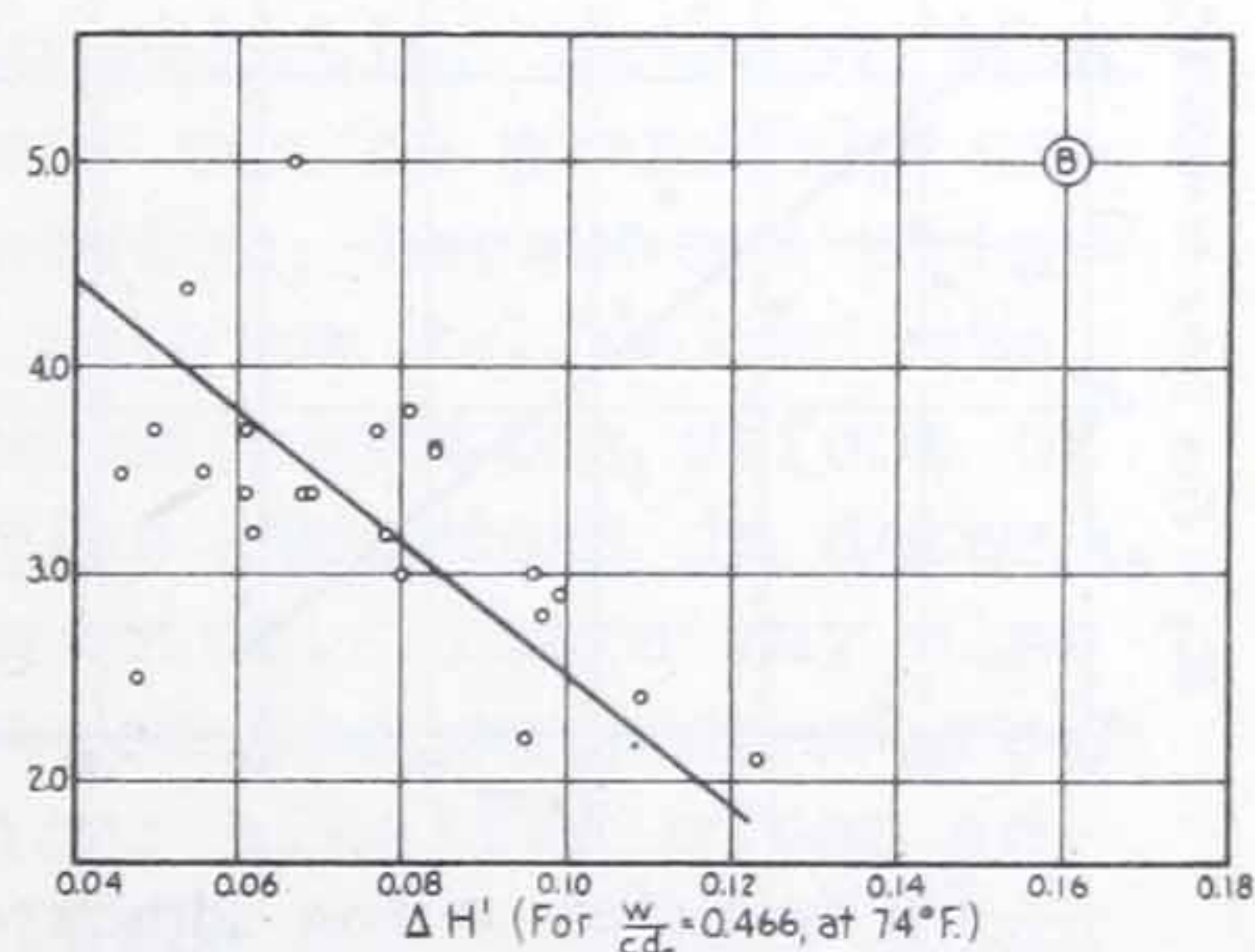
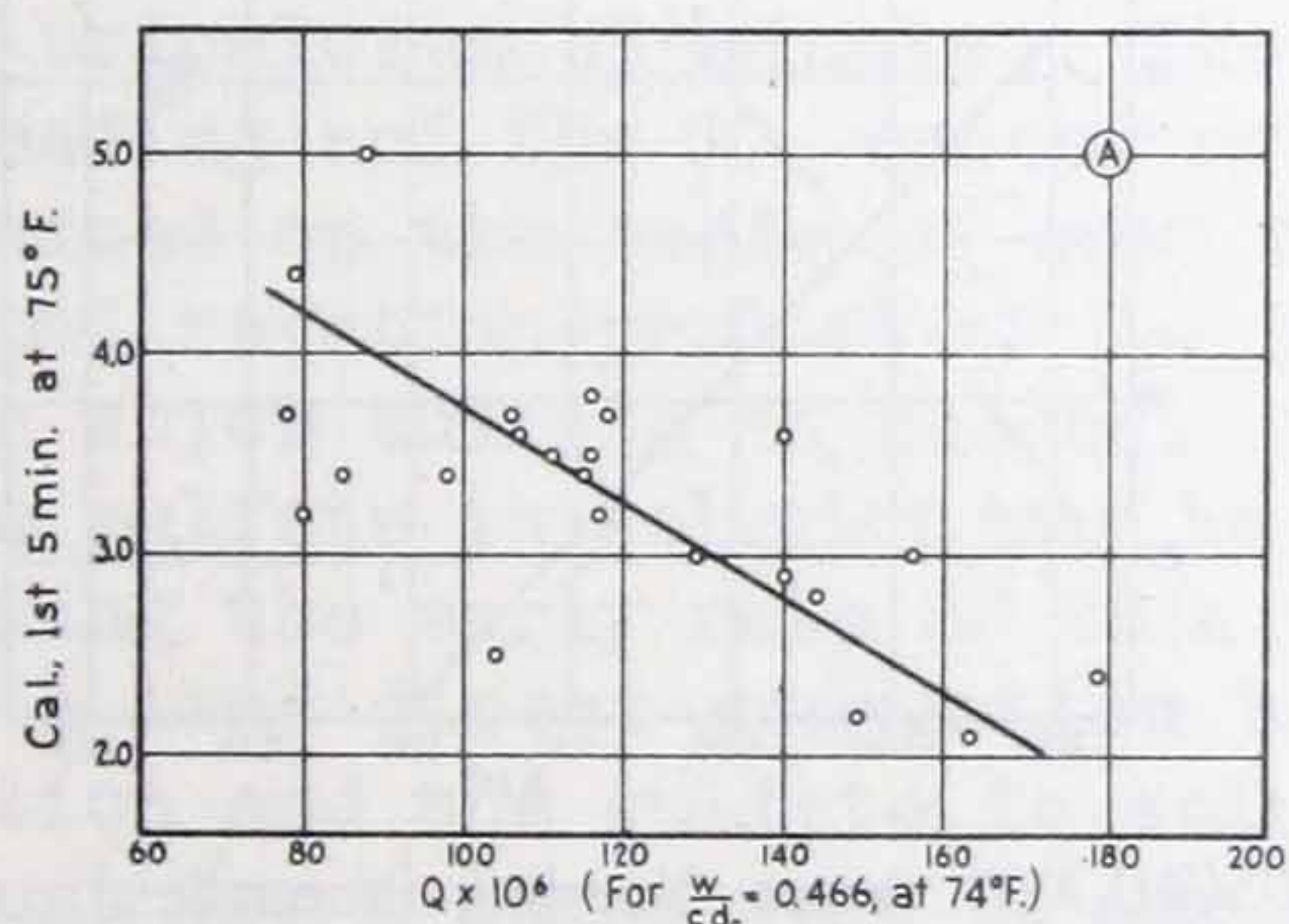


Fig. 14 - Heat Liberated in the First Five Minutes versus Bleeding Properties
(23 Cements)

- Ⓐ Correlation with bleeding rate
Coefficient of correlation: -0.70
Odds against chance correlation: 1035 to 1
- Ⓑ Correlation with bleeding capacity
Coefficient of correlation: -0.57
Odds against chance correlation: 127 to 1

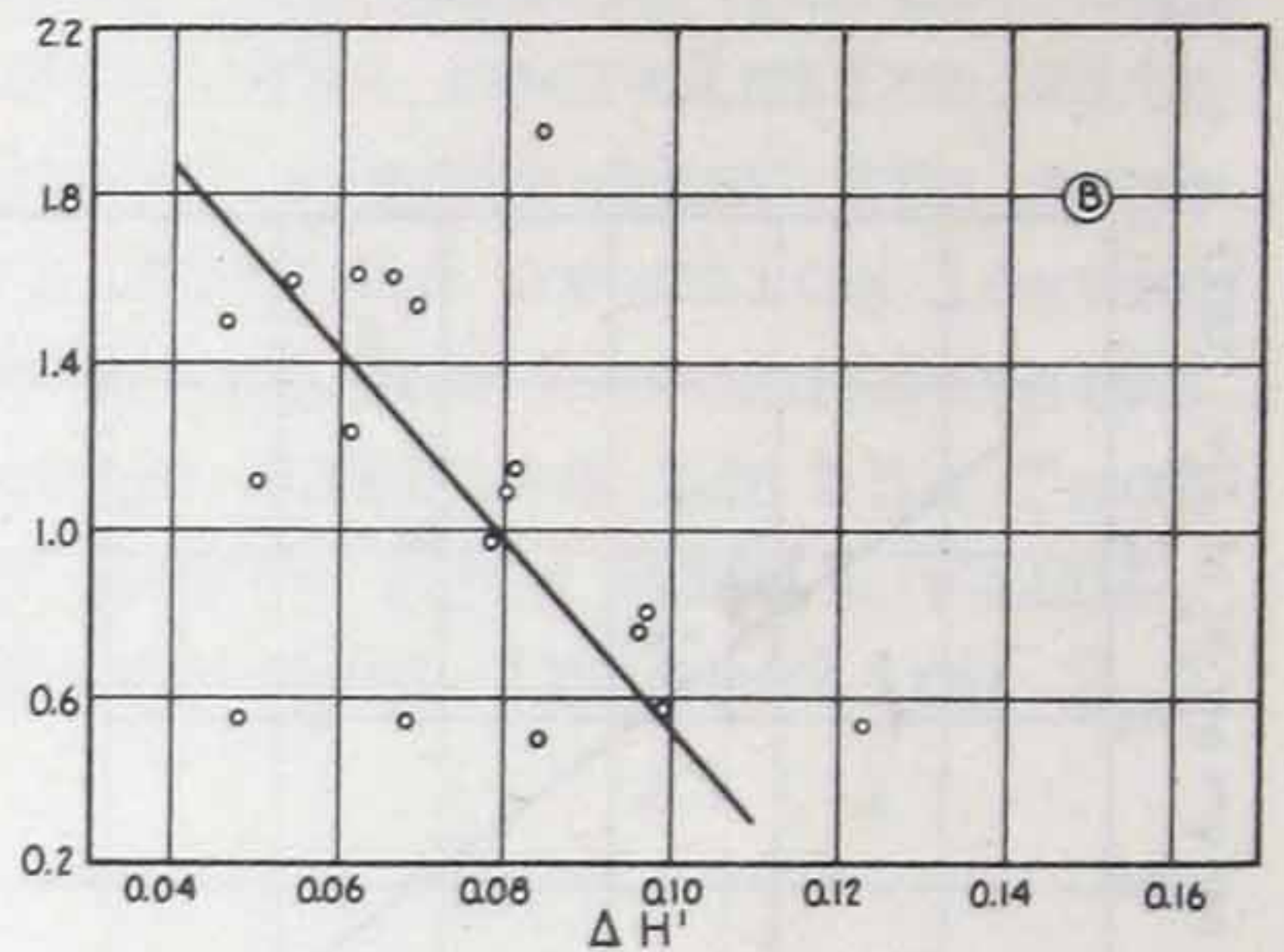
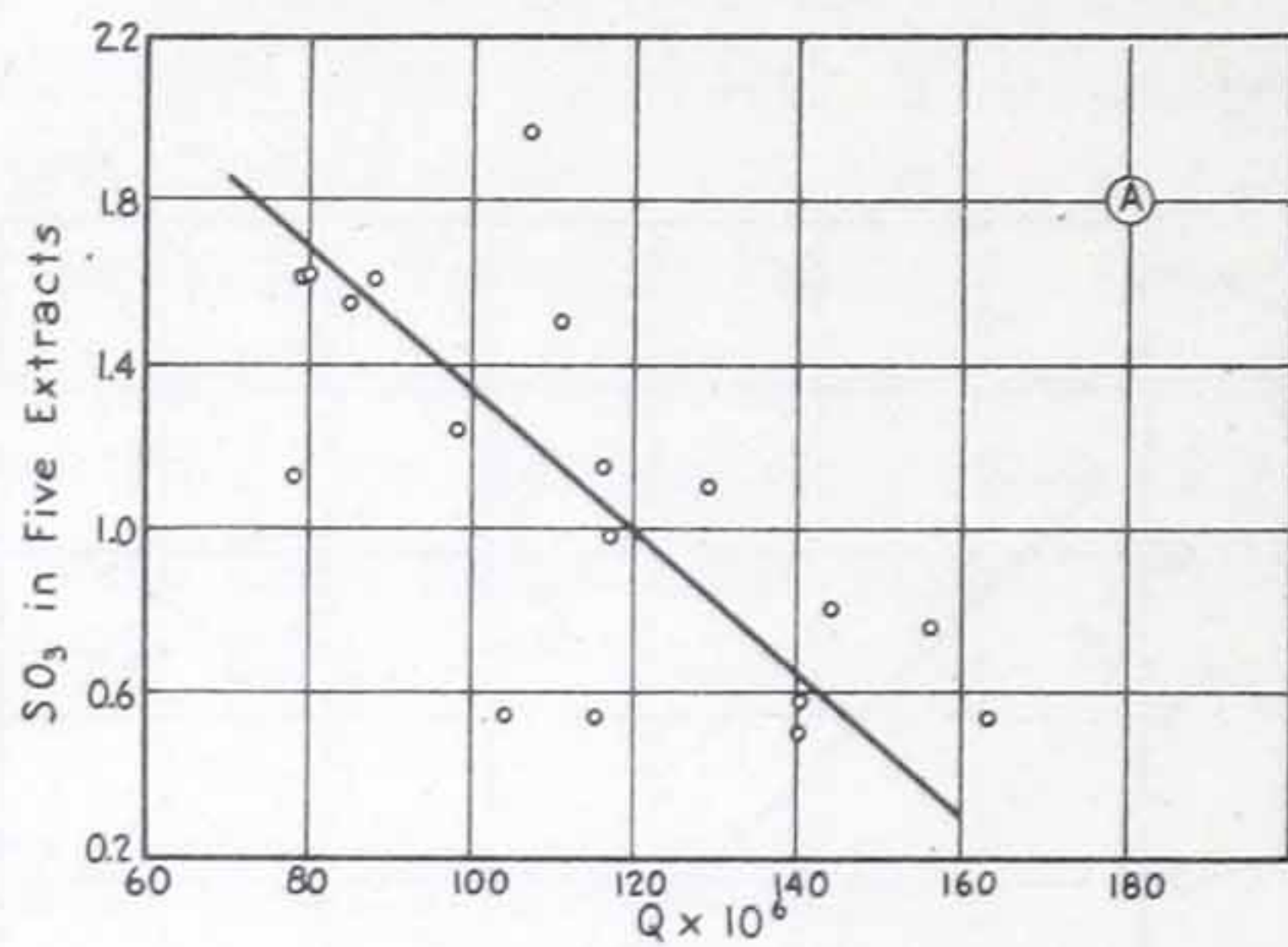


Fig. 15 - Sulfate in Five Extracts versus Bleeding Properties
(18 Cements)

- Ⓐ Correlation with bleeding rate
Coefficient of correlation: -0.70
Odds against chance correlation: 235 to 1
- Ⓑ Correlation with bleeding capacity
Coefficient of correlation: -0.43
Odds against chance correlation: 12 to 1

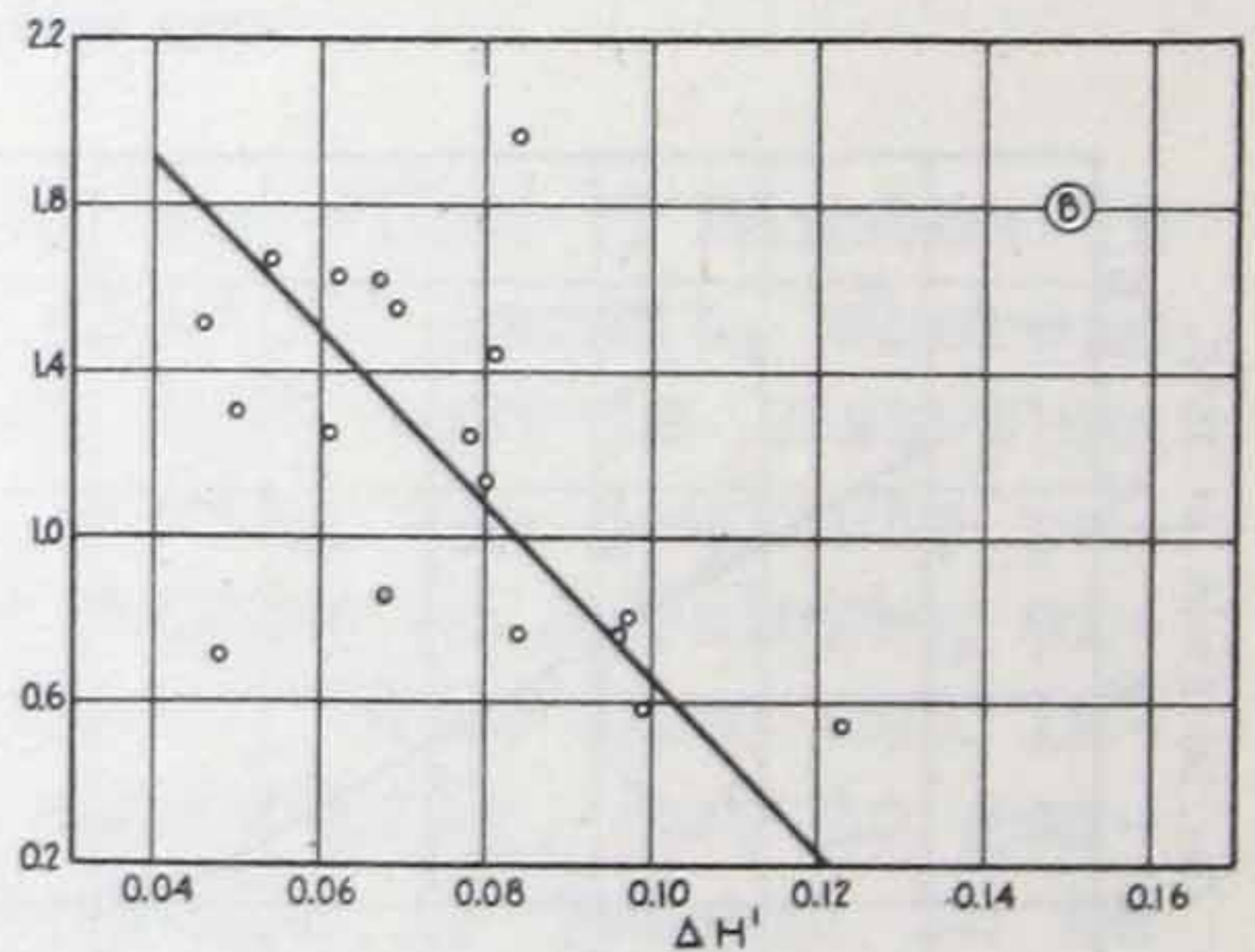
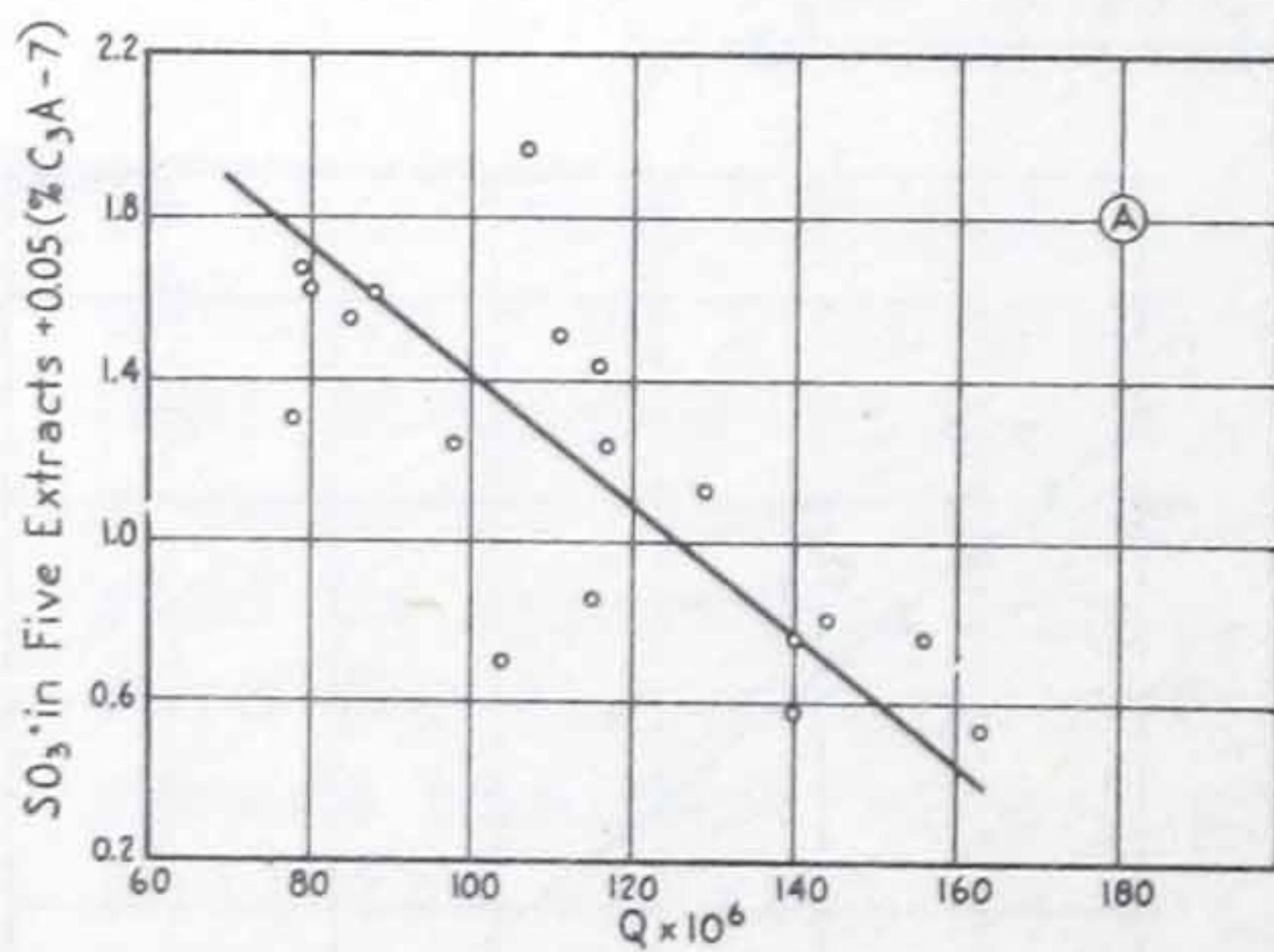


Fig. 16 - Sulfate in Five Extracts + 0.05(%C₃A-7) versus Bleeding Properties
(18 Cements)

- Ⓐ Correlation with bleeding rate
Coefficient of correlation: -0.76
Odds against chance correlation: 550 to 1
- Ⓑ Correlation with bleeding capacity
Coefficient of correlation: -0.51
Odds against chance correlation: 28 to 1

chance correlation are not as large as for the previous plots, but they can be materially improved by making an addition to the sulfate value when a cement is high in tricalcium aluminate. This is shown by Fig. 16 in which one-twentieth of the C_3A in excess of 7% was added to the SO_3 figures.

It will be noted that the data do not correlate as well with bleeding capacity as with bleeding rate. However, better correlation is obtained with other bleeding-capacity data, as is shown by Fig. 17. This, together with the fact that the correlations are of the same sign as those with the bleeding rate, gives reason to believe that the relationships are significant. It appears, however, that bleeding capacity is less closely related to the SO_3 concentration than is the bleeding rate.

The coefficients of correlation with the bleeding data are of such magnitude, both for the heat data and for the soluble SO_3 , as to indicate that the correlations result, in part at least, from a common cause. From the preceding discussion it appears that this underlying cause is chemical reaction, very probably reaction of tricalcium aluminate. The correlation between the bleeding and the SO_3 concentrations can be plausibly explained on the basis of such reaction, because a principal reaction-product of C_3A is calcium sulfoaluminate, for which sulfate is needed. The mass-action effect of the sulfate in solution may be quite important in determining the early rate of this reaction. There may also be a less direct connection between the extent of reaction and the sulfate in solution; alkalies often account for a large part of the soluble sulfate and Lerch (11) has concluded that alkalies in the cement probably increase the reactivity of the aluminates. The improvement in correlation that is brought about by weighting the SO_3 figure when the cement is high in C_3A tends of course to support the assumption that a reaction of C_3A is involved.

Soluble Alkalies

If the correlation between bleeding and extracted SO_3 is dependent in part upon effects of the alkalies, correlation between the bleeding and the amounts of dissolved alkalies is to be expected. That there is such correlation with respect to bleeding rate is shown by Fig. 18. It appears, however, that the correlation is not as good as that between the sulfate and the bleeding rate; hence, there is room for the opinion expressed above that the concentration of sulfate may directly affect the rate of formation of the calcium sulfoaluminate. Also, since dehydration of gypsum can supersaturate the solution with calcium sulfate, precipitation of gypsum may sometimes be a factor in reducing the bleeding, a factor which would contribute to the degree of correlation between the dissolved sulfate and the bleeding, but not to that between the alkalies and the bleeding. With respect to bleeding capacity, partial correlation with the alkalies is indicated, but the odds against chance correlation are too low to give confidence in the relationship.

Apparent Increase of the Density of Cement in Contact with Water

One of the properties that correlate well with the bleeding is an apparent increase in cement density caused by contact with water. The density determined in the usual way, in kerosene, is presumably correct. However, when water is used instead of kerosene, in a Le Chatelier flask or other type of pycnometer, the computed cement density is higher because interaction between the cement and water reduces the total volume. The pycnometer formula makes this appear as an increase in cement density. That this apparent increase in cement density (determined after about 20 minutes of contact between cement and water) is significantly related to the bleeding properties is shown by Fig. 19.

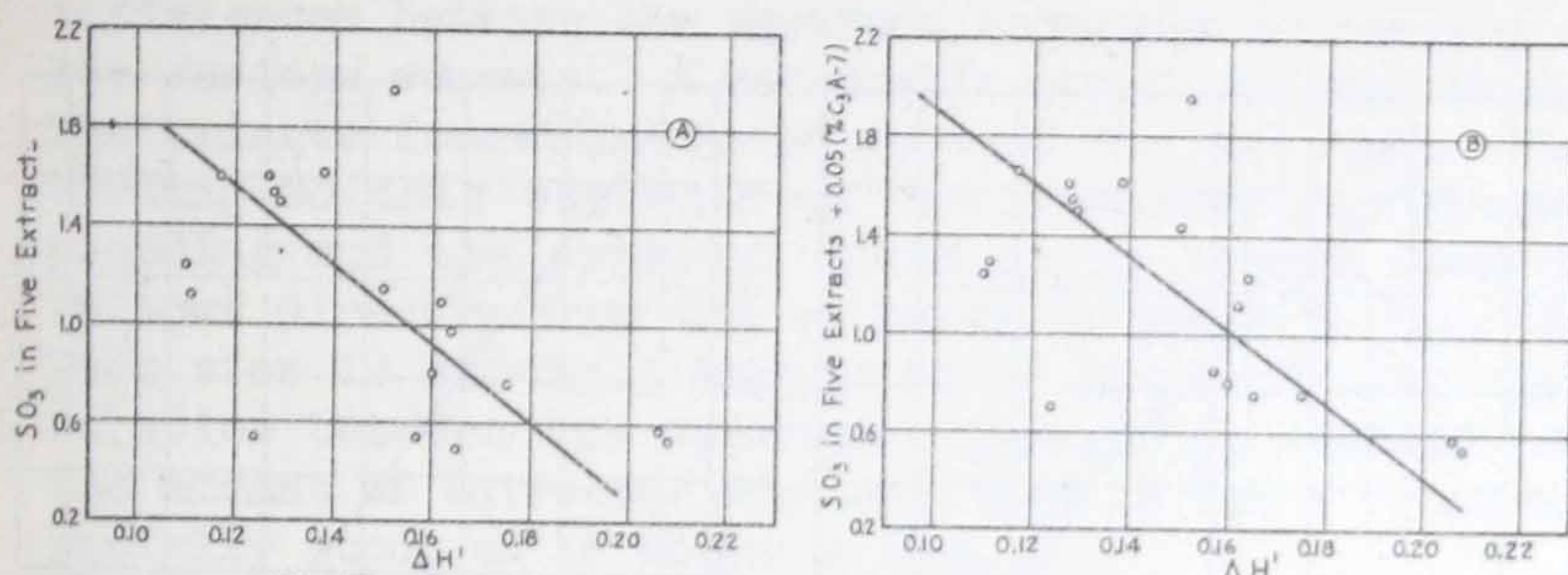


Fig. 17 - Relationships Between Extracted Sulfate and Bleeding Capacities for $\bar{w} = 2.0$, at 74° F. ($\frac{w}{c} = 0.63$) (18 Cements)

- Ⓐ Correlation between sulfate in five extracts and bleeding capacity
Coefficient of correlation: -0.58
Odds against chance correlation: 55 to 1
- Ⓑ Correlation between sulfate in five extracts + 0.05 (%C₃A-7) and bleeding capacity
Coefficient of correlation: -0.63
Odds against chance correlation: 103 to 1

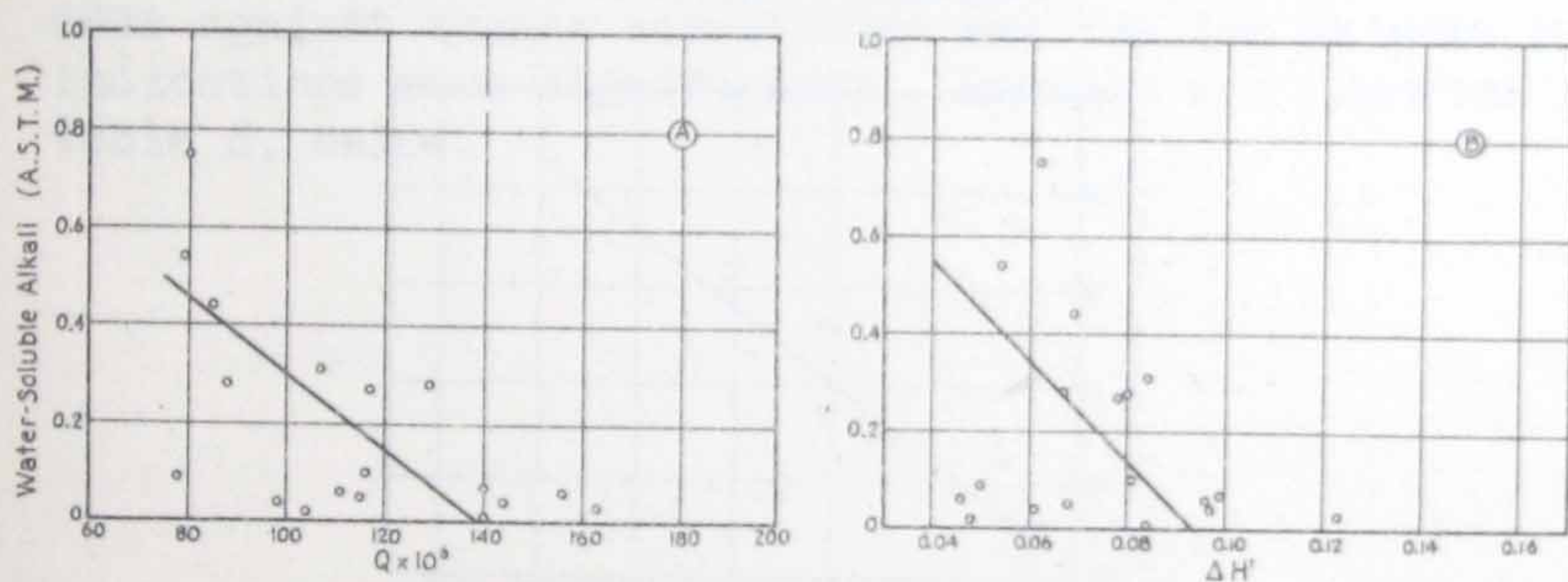


Fig. 18 - Water-Soluble Alkali (A.S.T.M.) versus Bleeding Properties (18 Cements)

- Ⓐ Correlation with bleeding rate
Coefficient of correlation: -0.61
Odds against chance correlation: 71 to 1
- Ⓑ Correlation with bleeding capacity
Coefficient of correlation: -0.27
Odds against chance correlation: 3 to 1

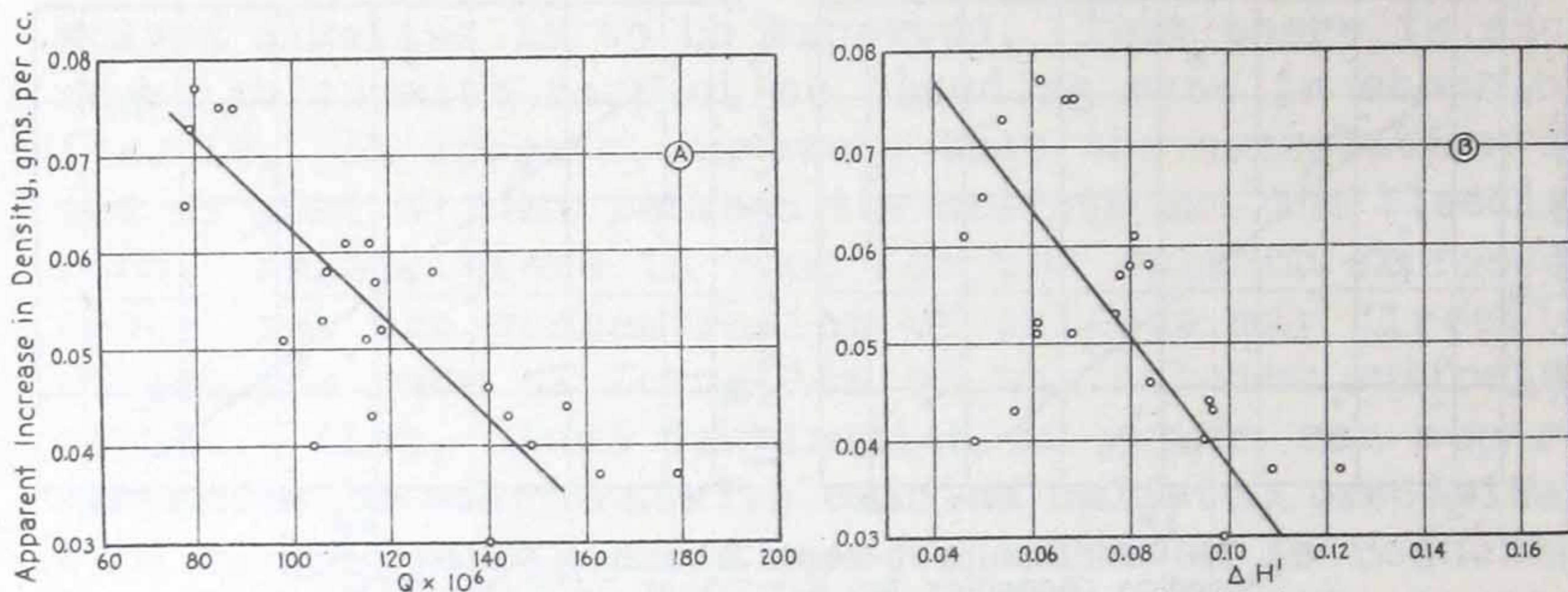


Fig. 19 - Apparent Increase in Density of Cement in Water versus Bleeding Properties (23 Cements)

- Ⓐ Correlation with bleeding rate
Coefficient of correlation: -0.80
Odds against chance correlation: 5440 to 1
- Ⓑ Correlation with bleeding capacity
Coefficient of correlation: -0.54
Odds against chance correlation: 92 to 1

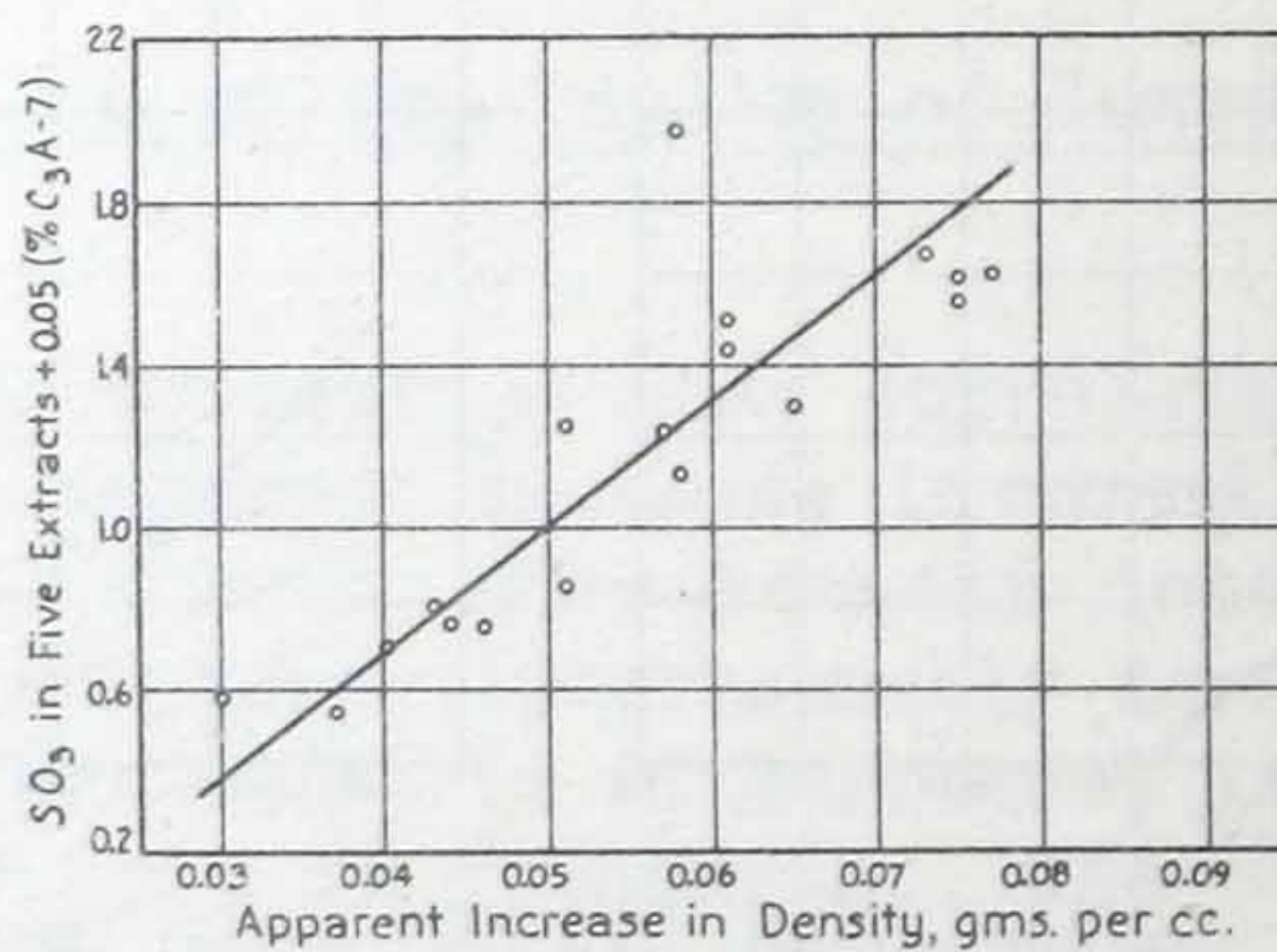


Fig. 20 - Sulfate in Five Extracts + 0.05 (%C₃A-7) versus Apparent Increase in Density of Cement in Water (18 Cements)

Coefficient of correlation: -0.86
Odds against chance correlation: 2700 to 1

From the proportions of cement and water used in the pycnometer test, the volume changes attending the solution of the sulfates can be estimated. It is found that they are sufficient to account for the major part of the differences between the apparent increases in density of the various cements. A reasonable amount of calcium sulfaluminate formation could account for the rest. According to this explanation the correlation between bleeding and the apparent increase in cement density follows directly from the correlation shown in Fig. 16. This view is strongly supported by the fact that correlation between the apparent increase in density and the amount of extracted SO_3 plus 0.05 ($\% \text{C}_3\text{A} - 7$) is especially good, as is shown by Fig. 20.

Other Properties

Among the tests that show wholly insignificant degrees of correlation with the bleeding rate are the Paul floc test and the Merriman sugar test. Both tests show some correlation with the bleeding capacity, but the odds against chance correlation are too low to give the indications much significance. Results are reported in Table 8, below.

Table 8

Some Results of Statistical Analysis

Test on Cement	Paul Floc Test	Merriman Sugar-Test	
		Phenol- phthalein End Point	Clear Point
No. of cements	23	23	23
Coefficient of correlation with bleeding rate:*	- 0.03	- 0.10	- 0.10
Odds against chance correlation with bleeding rate:	1 to 8	3 to 5	3 to 5
Coefficient of correlation with bleeding capacity:	- 0.30	- 0.40	- 0.40
Odds against chance correlation with bleeding capacity:	6 to 1	16 to 1	15 to 1

*The bleeding data used here are the same as in Fig. 13.

Summary

Correlation of bleeding data with data on heat liberation leaves little doubt but that the bleeding is materially affected by chemical reactions that occur when the cement is first mixed with water. Reactions of tricalcium aluminate are believed to be involved because of the relatively great reactivity and heat-producing capacity of this compound. Correlations between other properties and the bleeding are readily explained in terms of reaction of the aluminate. Apparently, the amount of the reaction-product is related to the amount of sulfate that goes readily into solution, and to a lesser degree to the amount of alkali in the cement, (which often supplies a considerable part of the soluble sulfate). The amount of the reaction product appears to increase with the amount of tricalcium aluminate in the cement when this is above 7%.

In general, the bleeding rate gives higher coefficients of correlation with other properties of the cement than does the bleeding capacity, but the coefficients have the same signs.

8. Miscellaneous Influences Affecting Bleeding Rate and Bleeding Capacity

The bleeding characteristics of a cement appear to be subject to as many influences as are other physical properties such as plasticity, setting time, and strength. Some miscellaneous information on these various influences has been assembled in this section.

Rate of Clinker Cooling

Employing methods somewhat different from that of Bulletin 2, William Lerch (10) showed that slow cooling of clinker can reduce the amount of bleeding. More recently, the method of Bulletin 2 has been used with two pairs of cements ground from quick and slow cooled clinkers. Some of the results are shown in Table 9. It is

evident that slow cooling can markedly reduce both bleeding rate and bleeding capacity, especially the latter.

Table 9

Bleeding Rate and Capacity As Affected by
Rate of Clinker Cooling

Paired cements are from a given raw mix.

Cement No.	Clinker Cooling	Sp. Surface, sq cm per gm (Turb. Air- Method) Permea- bility Method		w	Bleeding Rate Q x 10 ⁶	Bleeding Capacity, $\Delta H'$
14901	quick	1640	3030	0.59	184	0.092
14903	slow	1630	3070	0.59	123	0.042
14910	quick	1610	-	0.59	184	0.065
14912	slow	1640	-	0.59	109	0.024

Calcium Sulfate Retarder

In Bulletin 2 an increase in the proportion of gypsum in the cement was shown to have a large effect in reducing both bleeding rate and bleeding capacity even though the concentration of sulfate in solution did not vary much and the specific surface (by turbidimeter) was maintained practically constant. Subsequent tests have supported these findings. A simple explanation can now be given as a result of determinations of specific surface by the air-permeability method. It has been shown elsewhere (13) that the ratio of specific surface as determined by the air-permeability method to that as determined by the A.S.T.M. turbidimeter increases consistently with increase in the SO₃ content of the cement. Probably the air-permeability method gives the best account of the specific surface of the gypsum, since the

turbidimeter method does not analyze below $7\frac{1}{2}$ microns in particle-diameter.* Accordingly, when the specific surfaces, as determined by the turbidimeter, appear to be the same, the cements containing higher amounts of gypsum are probably actually finer and show lower values of Q and $\Delta H'$ for that reason.

However, gypsum can produce a more specific effect if it is partially dehydrated during milling. Lerch (10) investigated the effects of such dehydration and found that the bleeding capacity was greatly reduced, provided the paste was mixed for just 2 minutes. Longer mixing, conforming to the method of Bulletin 2, brought the bleeding capacity back almost to the same order of magnitude as was obtained when there was no dehydration. Lerch did not study bleeding rate, but more recent tests made according to the method of Bulletin 2 indicate that the dehydration causes a pronounced reduction in the rate. The tests were made on ground clinker, with the addition of plain gypsum in one case, and the same gypsum, partially dehydrated, in the other. The results are shown in Table 10.

In further work, a cement ground in the laboratory was compared with a commercial cement that was believed to contain dehydrated gypsum. In the laboratory grind, some of the same clinker was used and practically the same fineness was produced without dehydration of the gypsum. The results of bleeding tests, shown in Table 11, are comparable to those in Table 10.

*Other factors that affect the accuracy of the turbidimeter analysis are the differences in density and in opacity between gypsum and clinker.

In other tests a limestone powder was mixed with plain gypsum in one case, and with dehydrated gypsum in another. The preparation containing the dehydrated gypsum gave much the lowest bleeding rates and bleeding capacities. Apparently, pronounced dehydration of the gypsum always tends to reduce the bleeding rate. Whether it reduces the bleeding capacity depends upon the mixing schedule, and perhaps upon other circumstances also.

Table 10

Bleeding Data for Ground Clinker
No. SBR - 16065 at $w = 0.65$

Retarder	Bleeding Rate $Q \times 10^6$	Bleeding Capacity, $\Delta H'$
Dehydrated gypsum	204	0.085
Plain gypsum	280	0.085

Table 11

Bleeding Data at $w = 0.575$

Cement	Bleeding Rate $Q \times 10^6$	Bleeding Capacity, $\Delta H'$
Mill cement SBR - 15667 believed to contain dehydrated gypsum	230	0.128
Lab. grind from same clinker as cement SBR - 15667	298	0.131

Aeration of Cement

Lerch (10) found that alkali carbonates such as might be formed by aeration of cement greatly reduced the bleeding capacity of a paste mixed only 2 minutes. Longer mixing increased the bleeding capacity but failed to bring it back to the original value when admixed Na_2CO_3 amounted to 0.5% or more.

Some cements tested according to the method of Bulletin 2 have shown large reductions in bleeding rate and bleeding capacity after storage for a few months in partly filled containers that were not air-tight. Sometimes only the one or the other property was affected.

Salts

In Bulletin 2 it was indicated that dissolved salts reduce the bleeding rate and may also reduce the bleeding capacity. Many tests have been made since then involving various cements and various alkali salts, but chiefly sodium chloride. The salts always reduced the rate but generally had little effect on the bleeding capacity. Special tests indicated that the effect on the rate was less if the gypsum in the cement was strongly dehydrated. Reductions in rate were commonly somewhat less than those found in the tests reported in Bulletin 2, especially at the lower concentrations of salt. A retest of cement 14502, which had supplied data for Bulletin 2, showed a very much diminished effect, indicating some change during storage. A few of the data for other cements are given in Table 12.

Table 12

Effect of Sodium Chloride in 1 Normal Solution
(a 5.6% solution)

Cement No.	NaCl in Mix Water	w	Bleeding Rate, $Q \times 10^6$		Bleeding Capacity, $\Delta H'$
			Actual	Calculated for same density and viscosity as pure water	
SBR-15621	none	0.62	224		0.082
	5.6%	0.62	177	195	0.069
SBR-15931	none	0.60	151		0.089
	5.6%	0.60	103	134	0.083
SBR-15668	none	0.63	270		0.148
	5.6%	0.63	220	243	0.148
SBR-15667*	none	0.55	167		0.099
	5.6%	0.55	151	166	0.105

*Believed to have contained dehydrated gypsum.

As was noted in Bulletin 2, calcium chloride produces larger effects per chemical equivalent than the alkali salts. Some recent data on the effect of calcium chloride are shown in Table 13. It is evident that the bleeding capacities are more strongly reduced than the initial bleeding rates. This, together with the fact that the calcium chloride also greatly reduces the bleeding time, supports the view expressed in Bulletin 2 that the influence of the calcium chloride may be largely the effect of its known acceleration of setting. It is of interest in this connection that the constant-rate periods tended to be rather brief when the calcium chloride was present. Another effect of the calcium chloride was to make the cements more susceptible to channeling.

Table 13

Tests with and without Calcium Chloride
Equal to 1% of the Weight of Cement (about
2.1% of the water)

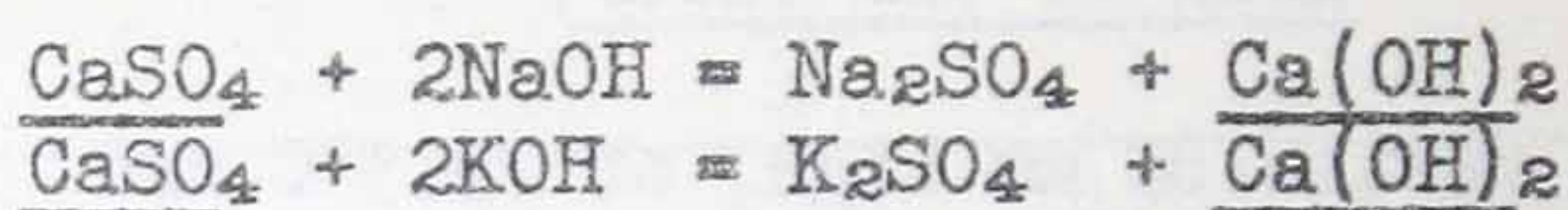
Tests on pastes 60 mm high, at 23.5°C and
 $w = 0.60$, except for cement SBR-15668 which was
 tested at $w = 0.575$.

Cement No.	Addition	Bleeding Time, min.	Bleeding Rate, $Q \times 10^6$		Bleeding Capacity $\Delta H'$
			Actual	Calculated for same density and viscosity as pure water	
SBR-15365	none	71	163		0.085
	CaCl ₂	38	146	156	0.040
SBR-15496	none	46	129		0.049
	CaCl ₂	26	89	95	0.020
SBR-15621	none	71	139		0.072
	CaCl ₂	46	103	110	0.039
SBR-15697	none	81	122		0.077
	CaCl ₂	58	94	100	0.047
SBR-15668	none	87	156		0.093
	CaCl ₂	71	122	131	0.068

Alkali Hydroxides

It was previously reported (in Bulletin 2, p. 51) that bleeding rate is not affected by sodium hydroxide in solution. This matter has been further investigated using two cements, both of which were low in alkali oxides (less than 0.35%). The initial solutions were 1/8, 1/4, and 1 Normal in alkali hydroxide, and both NaOH and KOH were used, in different tests. After mixing the

solutions with the cement, the hydroxide concentrations fell markedly because a high concentration of alkali hydroxide reacts with gypsum and precipitates hydrated lime, as shown by the following equations:*



When the weaker solutions (1/8 and 1/4 Normal) were used, the bleeding rates and bleeding capacities were not strongly affected; but there was, in some cases, an appreciable increase in rate and decrease in bleeding capacity. The 1 Normal hydroxide reduced the bleeding rate, but no more than corresponded to the greater density and viscosity of the liquid. It materially reduced the bleeding capacities of both cements, but the effect was much greater for one cement than the other. As the cement most affected was high in C₃A whereas the other was not, it seems likely that the reduction of the amount of retarder by reason of the reaction cited above may have caused the difference in results. Some of the bleeding data obtained with the cement on which 1 Normal hydroxide had the least effect on the bleeding capacity are shown in Table 14.

The tendency of the 1 Normal hydroxide to reduce the bleeding capacity while producing no specific effect on the bleeding rate is analogous to results obtained with silica powder when the concentration of flocculant is increased (See Bulletin 2, p. 72). To study the possibility that the hydroxide affects the state of flocculation, some auxiliary tests were made in small vials using 2 grams of cement to 10 ml of water or solution. A 1/2 Normal solution of NaOH caused the sediment to occupy more than twice the volume that it had in tap water, and the supernatant liquor was brilliantly clear, whereas it was not when tap water was used. Other concentrations also gave

*Confirmed by analysis of the paste liquor.

Table 14

Effect of Alkali Hydroxides on Cement No. SBR-15668
(23.5°C)

Solution	w	Bleeding Rate, $Q \times 10^6$		Bleeding Capacity, $\Delta H'$
		Actual	Calculated for same density and viscosity as pure water*	
water	0.575	161		0.105
1/8 N. NaOH	"	164		0.105
1/4 N. NaOH	"	152		0.096
1 N. NaOH	"	123	157	0.067
1/8 N. KOH	"	162		0.086
1/4 N. KOH	"	164		0.083
water	0.063	260		0.160
1/8 N. NaOH	"	283		0.169
1/4 N. NaOH	"	277		0.153
1 N. NaOH	"	211	270	0.086
1/8 N. KOH	"	297		0.142
1/4 N. KOH	"	304		0.143
1 N. KOH	"	219	251	0.079

*The correction is relatively small for the 1/8 and 1/4 N solutions. Since it is a slight over-correction with respect to cement liquor, which is not pure water, it was not applied to these weaker solutions.

volumes of sediment greater than in tap water, but the $\frac{1}{2}$ Normal solution showed the greatest effect. In no case did the sediment "set" during the tests. It is believed that the alkali hydroxides probably do affect the state of flocculation, and that the hydroxyl ion, which can be supplied by calcium hydroxide also, may perhaps act directly as the flocculant. The cement particles in a paste are normally positively charged in spite of the fact that the paste is flocculated*; perhaps it is the negative hydroxyl ion that keeps the charge sufficiently low to permit of the flocculation.

Temperature During Test

Tests reported in Bulletin 2 showed that with increase in temperature a reduction in rate of bleeding began at about 25°C in spite of the decrease in viscosity of the water with temperature. At lower temperatures the rate varied in inverse proportion to the viscosity of the water as would be expected from Equation 2 if w_1 remained constant. Because of the unexplained reduction in rate at the higher temperatures, most of the subsequent bleeding tests have been made at about $23.5 \pm 1^\circ\text{C}$. However, because cements are often used at higher temperatures the cements of the LTS group have been tested at two different temperatures, namely, 23.5°C and 32°C (74°F and 90°F). At both temperatures enough tests on each cement were made at a water-cement ratio of 0.466, by weight, to establish the bleeding rates and bleeding capacities rather well. The data are shown in Table 15. It is evident that in most cases the bleeding rates increased with temperature, and that the cement which gave the data reported in Bulletin 2 was therefore not representative of cements in general.

The ratios of the bleeding rates for 32°C to those for 23.5°C would have been 1.20 had the change in rate with change in temperature resulted only from the change

*This was shown by electroosmosis in tests that the writer made for the Riverside Cement Co. The reference is to pastes not over 7 hours old.

Table 15

Bleeding Data for Cement Pastes at 23.5°C, and 32°C

(Water-cement ratio, by weight = 0.466)

Cement No. (LTS group)	Initial Bleeding Rate, $Q \times 10^6$			Bleeding Capacity, $\Delta H'$		
	23.5°C	32°C	32° values	23.5°C	32°C	32° values
			23.5° values			23.5° values
11 - 616	120	134	1.12	0.080	0.065	0.81
11T- 717	62	-	-	0.030	-	-
12 - 625	120	160	1.33	0.084	0.081	0.96
12T- 726	127	80	0.63	0.038	0.046	1.21
13 - 621	134	159	1.19	0.062	0.053	0.85
14 - 423	75	66	0.88	0.050	0.042	0.84
15 - 526	130	170	1.31	0.079	0.080	1.01
16 - 834	139	167	1.20	0.086	0.083	0.96
16T- 835	115	131	1.14	0.069	0.067	0.97
17 - 640	86	120	1.40	0.059	0.067	1.13
18 -2044	130	-	-	0.078	-	-
18T-3025	105	115	1.10	0.044	0.023	0.52
21 - 223	190	217	1.14	0.120	0.120	1.00
21T- 310	120	151	1.26	0.085	0.079	0.93
22 - 618	141	176	1.25	0.053	0.076	1.43
23 - 521	148	173	1.17	0.091	0.090	0.99
24 - 631	71	60	0.84	0.053	0.042	0.79
25 - 655	109	130	1.19	0.086	0.085	0.99
31 - 628	35	46	1.31	0.015	0.012	0.80
33 - 430	54	57	1.06	0.025	0.023	0.92
33T- 511	36	53	1.47	0.015	0.017	1.13
34 - 621	60	71	1.18	0.029	0.029	1.00
41 - 660	76	86	1.13	0.061	0.056	0.92
42 - 630	146	162	1.11	0.114	0.112	0.98
43 - 722	75	93	1.24	0.053	0.056	1.06
43A- 322	89	112	1.26	0.053	0.050	0.94
51 - 532	112	183	1.63	0.077	0.111	1.44

A "T" in the cement number indicates a so-called "treated" cement, that is, an air-entraining cement made by addition of Vinsol resin.

in viscosity of the water. For the 20 cements in Table 15 that were made without Vinsol resin and for which data are available at both temperatures (that is, not counting cement No. 18) the average ratio is 1.20 and the ratios for 14, or 70%, of these cements are within 10% of the theoretical value. It appears that in most cases the theoretical rate-equation, with about the same value of w_i , remains applicable as the temperature is raised considerably above 23°C. However, some cements do not conform at all well, and this is probably attributable to changes either in the amount of early chemical reaction or in the state of flocculation.

The ratios of the bleeding capacities at the two test temperatures average 0.99 for the same 20 cements, and 12, or 60%, of these ratios are within 10% of 1.00. In general, therefore, there was little change in bleeding capacity with the change in temperature, but again there were some pronounced exceptions to the general rule.

Vinsol Resin

The air-entraining cements of the LTS group were all made by addition of Vinsol resin (about 0.04%) during the grinding. Cements made at the same plants from the same clinkers but without this addition provide a good basis for judging the effect of the resin. In Table 15, cements made from the same clinker are indicated by the same number in advance of the hyphen, except for the T, which designates the air-entraining cements. Table 15 contains only a few of the bleeding data which are available for comparison.

In Bulletin 2 a method is given for estimating the effect of air-entraining admixtures like Vinsol resin on the bleeding rate of a cement. According to this method the entrained air is treated as a weightless aggregate of negligible surface exposure. Results obtained with an air-entraining agent were shown in Bulletin 2 to agree rather well with the calculated values. Similar

calculations were made for the treated, or air-entraining, cements of the LTS group, but the agreement was not always good. The principle of the calculation is believed to be valid, but evidently something more is sometimes involved.

The entrained air generally reduces the bleeding capacity by more than can be accounted for by the volume occupied by the air itself. Air contents of the pastes of Table 15 that were made with treated cements were found experimentally to range from 1.2% for cement 11T to 13.2% for cement 16T.

9. Summary and List of Factors That Affect the Bleeding of Cement Paste

1. Subsequent experimental and theoretical studies have supported, in general, the views on the mechanism of the bleeding of cement paste that were presented in P.C.A. Bulletin 2. However, because of minor revisions of theory, the equation for initial bleeding rate that was developed in Bulletin 2 now appears to represent certain basic influences rather less precisely than was at first thought. Nevertheless, it provides a sufficiently accurate representation of experimental data.

The later work has supported the previous explanation that w_i , the experimental constant of the rate equation, is required because a part of the water remains immobile with respect to the cement particles, i.e., does not flow past them during the bleeding. However, w_i is now considered to be only an indirect measure of the quantity of such water. Also, most of this water is now believed to be present in "dead" spaces caused by the angularity of the particles, rather than in thick, solvated layers bound to the particles, as was previously considered probable. However, it is thought that thinner layers, of hydration products, probably do form around the cement particles when they first contact water, and are largely responsible for the differences between the w_i values. Support for this latter view is found in the correlation of the data

on bleeding with the initial heat liberation, and with compositional factors.

2. The fact that a cement paste is flocculated is now given more emphasis than formerly, especially in analyzing the influences that affect the bleeding capacity. New experimental studies have led to revision of the equation relating the bleeding capacity to the water content of the paste. The following equation, though purely empirical, appears to be generally satisfactory:

$$\Delta H' = k^2 c [w/c - (w/c)_m]^2$$

The symbols are defined in the nomenclature list at the end of this report. The equation gives a straight line when $\sqrt{\Delta H'/c}$ is plotted against w/c .

3. The rather extensive bleeding data now available have been analyzed with respect to the influence of cement fineness, the relationship between bleeding rate and bleeding capacity, and the duration of bleeding. The earlier indications regarding the strong influence of the cement fineness on the bleeding characteristics have been confirmed; reduction in water content and increase in cement fineness are, in general, the most important ways of reducing the bleeding of normal, untreated portland cement paste. Bleeding rates and bleeding capacities have been shown to be closely related but, when different cements are concerned, a difference in rate is by no means an infallible indication of a difference in bleeding capacity. Duration of bleeding has been found to be remarkably insensitive, in many cases, to the water content of the paste.

4. Among miscellaneous influences, the effect of the temperature of the paste has received further study. Tests on many different cements have now been made both at 74 and 90°F. Most cement pastes show about the same bleeding capacity at both temperatures, and they change in bleeding rate to about the extent that corresponds to

the change in viscosity of the water. However, a considerable number of cements change their bleeding characteristics with change in temperature in a way which is unpredictable at present though probably related to the amount of initial reaction, and perhaps also to the state of flocculation.

5. Tests of cements treated with Vinsol resin indicate that the effect of the entrained air is not always fully predictable simply on the basis that the air is weightless aggregate. The entrained air generally reduces the bleeding capacity of the paste by more than the volume occupied by the air.

6. On the basis of the information now available, it is possible to list a considerable number of factors that affect the rate and amount of bleeding of a cement paste. Important among the test conditions are, of course, the water content and the temperature of the paste. Factors that relate to the composition, production, or storage of the cement are listed below. Although the magnitudes are so expressed that lowering of the bleeding rate and bleeding capacity is the effect that is indicated, it will be evident that some of the factors could be varied in magnitude in such manner as to increase bleeding.

Factors That Can Lower
Bleeding Rates and Bleeding Capacities
of Cement Pastes

- high soluble alkali in clinker
- high C_3A in clinker
- slow cooling of clinker
- high cement fineness
- large addition of gypsum
- hot milling
- addition of an air-entraining agent
- addition of calcium chloride
- exposure of cement to the air

This is not to be regarded as a complete list of all factors that can influence the bleeding. It covers only those factors on which enough evidence has been obtained to warrant mention at this time.

Nomenclature

- c = absolute volume of cement per unit volume of mix
 c_B = maximum volume of cement per unit of settled volume
(the maximum obtainable with a given cement)
 d_c = density of cement, gm/cm³
 d_f = density of water, gm/cm³
 g = the gravitational acceleration, cm/sec², (about 980)
 $\Delta H'$ = bleeding capacity. It is the ratio of the total decrease in paste height to the initial paste height.
 k = the slope of the data line in a plot of $\sqrt{\Delta H'/c}$ versus w/c
 Q = bleeding rate, cm/sec. It is the initial rate of settlement of the top surface of the paste.
 R = the ratio of the actual bleeding time to the time in which the same settlement would have occurred had the initial rate prevailed throughout
 V_s = a velocity calculated by applying Stokes' law, expressed in terms of σ , to a given powder, irrespective of whether the particles are of uniform size
 w = volume of water per unit volume of mix ($w+c = 1$)
 w_B = minimum volume of water per unit of settled volume ($w_B + c_B = 1$)
 w_1 = a term (used in equations for bleeding rate) which has a constant value for a given cement tested at a given temperature. It is a correction for water not involved in the flow but does not represent directly the quantity of such water.
 $(w/c)_m$ = minimum water-cement ratio (by absolute volume) for pastes of a given cement. It is determined by Equation 7.
 N = Number of pairs of data
 η = coefficient of viscosity of water, gm/cm sec, (poises)
 σ = specific surface of cement (on volume basis), cm²/cm³
 σ_w = specific surface of cement (on volume basis), cm²/cm³, as determined in accordance with the Wagner turbidimeter method, A.S.T.M. Designation C115-42

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Appendix A

Chemical Constitution

The chemical constitutions of the clinkers from which were produced the cements having the group designation SBR* are given in Table 16. The cements contained amounts of SO_3 which varied only from 1.73 to 2.11%, except for 2.48% in Lot SBR-15365, and 1.59% in Lot SBR-15622. The specific surfaces of the cements are reported, along with the bleeding data, in Appendix B which gives the serial numbers of the cements produced from each clinker.

Since most of the cements of the LTS group were ground from different clinkers, the chemical constitutions of the cements (rather than of the clinkers) are given for this group, in Table 17. Cements having the same identification except for a T were produced at the same plants, and from clinkers of approximately the same constitutions. The T designates air-entraining cements produced by addition of Vinsol resin.

*With respect to group-designations see page 2.

Table 16

Chemical Constitution of Clinkers from which
the Cements of the SBR Group were Produced

The compounds were computed on the potential compound basis without correction of the CaO, SiO₂, Al₂O₃, and Fe₂O₃ analyses, except for subtraction of the free lime from the total CaO. The letters C, S, A, and F are used to represent the oxides in the formulas for the four major compounds.

Clinker Ref.No.	C ₃ S %	C ₂ S %	C ₃ A %	C ₄ AF %	MgO %	Free CaO %	SO ₃ %	Alkali Loss on Oxides, Ign., %*	
1	46.5	27.6	14.3	6.8	2.6	1.0	0.4	0.3	0.2
2	62.9	12.6	11.1	7.7	1.4	2.7	0.2	0.7	0.9
3	47.6	30.9	4.8	13.2	1.4	0.7	0.0	0.2	1.1
4	37.1	52.2	2.3	5.7	1.8	0.2	0.2	0.3	0.3
5	48.4	28.7	10.1	7.6	3.4	0.0	0.2	1.6	0.4

*Taken from cement analyses.

Table 17

Chemical Constitution of Cements
of the LTS Group

The compounds were computed on the potential compound basis without correction of the CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 analyses, except for subtraction of the free lime from the total CaO . The letters C, S, A, and F are used to represent the oxides in the formulas for the four major compounds.

Cement No.	C_3S %	C_2S %	C_3A %	C_4AF %	MgO %	CaSO_4 %	Free CaO %	Alkali Oxides %	Loss on Ign., %
LTS-11	51.0	21.0	12.1	7.2	3.6	2.7	0.4	0.7	1.0
LTS-11T	51.0	21.0	12.2	7.1	3.7	2.6	0.5	0.7	1.2
LTS-12	45.0	28.0	12.6	7.3	3.1	2.7	0.1	0.7	0.6
LTS-12T	46.0	27.0	12.5	7.1	3.1	2.7	0.1	0.7	0.7
LTS-13	50.0	26.0	10.1	6.5	1.1	2.8	1.6	0.2	1.8
LTS-14	42.5	32.0	8.2	9.2	2.5	2.9	0.2	1.4	0.9
LTS-15	64.5	10.0	12.1	7.5	0.8	3.2	0.4	0.3	0.9
LTS-16	53.5	21.0	7.5	10.7	2.0	2.9	0.7	0.7	1.0
LTS-16T	52.5	22.0	7.9	10.4	2.0	3.1	0.8	0.7	1.2
LTS-17	52.0	23.0	10.4	9.3	1.1	2.9	0.4	0.5	0.9
LTS-18	44.5	28.0	13.2	6.8	2.1	3.1	0.3	0.3	1.0
LTS-18T	44.0	28.5	13.2	6.7	2.1	2.9	0.4	0.3	0.9
LTS-21	40.0	41.0	6.4	9.7	1.3	2.1	0.6	0.6	0.7
LTS-21T	38.0	40.0	6.6	9.7	1.3	2.2	0.6	0.6	0.6
LTS-22	41.5	33.5	6.6	11.7	3.2	2.4	0.1	0.6	0.6
LTS-23	51.0	24.0	3.7	16.6	0.9	2.6	0.4	0.7	0.6
LTS-24	41.0	29.0	5.4	14.8	3.1	3.0	0.9	1.4	1.4
LTS-25	34.0	39.0	4.7	14.9	2.2	3.2	0.2	0.8	0.6
LTS-31	56.0	17.0	10.8	6.4	3.3	3.8	1.4	0.5	1.5
LTS-33	60.0	13.0	10.4	7.7	1.4	3.9	1.8	0.7	1.5
LTS-33T	57.0	16.0	10.4	7.3	1.5	3.7	1.8	0.7	1.4
LTS-34	64.0	10.5	5.7	10.1	2.5	2.9	2.3	0.6	1.5
LTS-41	20.0	51.0	4.5	15.2	3.0	3.4	0.4	1.3	1.3
LTS-42	27.0	55.0	3.5	8.2	1.8	2.6	0.2	0.4	0.9
LTS-43	25.0	48.0	6.2	13.8	1.6	3.6	0.1	1.1	0.7
LTS-43A	29.0	52.0	5.3	9.3	1.1	3.2	0.4	0.3	0.8
LTS-51	41.0	39.0	3.7	10.0	1.7	2.4	0.5	0.3	0.8

Appendix B

Bleeding Data for Pastes Made with Cements of the SBR Group

In this appendix are presented all the data from an extensive series of bleeding tests made when the cements of the SBR group were first received. The cements have been studied systematically with respect to many properties; the bleeding data reported here were obtained not only for the independent study of bleeding but to make comparisons with the other properties of the cements. The bleeding characteristics of the cements of the LTS group were determined with similar objects in mind. However, they are not given here since Tables 3, 6, and 15 of the main report are considered adequate for present purposes.

The cements of the SBR group for which data are presented here were ground at the plants. However, when cements of four finenesses are represented, some were obtained by mixing. The data are in Table 18. The total bleeding times are shown only for those tests in which the times were determined to within 5 minutes.

Table 18

Bleeding Data for Pastes made
with Cements of the SBR Group

Cement No.	Clinker No.	Specific Surface cm^2/gm^*	Cement Content of Paste c	Paste Temp., $^{\circ}\text{C}$	Height of Paste, mm	Bleeding Rate $Q \times 10^6$	Bleeding Capacity, $\Delta H'$	Bleeding Time, min.
SBR-15364	1	1040	0.543	24.0	44.0	92.5	0.037	45
			0.522	23.0	46.5	118.0	0.045	40
			0.503	24.5	46.0	158.0	0.064	46
			0.483	24.0	47.0	208.0	0.080	45
			0.483	23.3	47.0	249.0	0.085	40
			0.457	23.4	47.0	263.0	0.104	45
SBR-15365	1	1665	0.482	23.7	58.0	59.2	0.025	55
			0.432	24.4	55.5	103.0	0.045	55
			0.382	22.8	55.0	189.0	0.104	76
			0.330	22.4	55.0	312.0	0.173	71
SBR-15366	1	2280	0.480	25.0	58.0	27.9	0.007	36
			0.430	25.0	49.0	46.6	0.016	38
			0.380	24.5	57.0	82.2	0.035	50
			0.350	24.5	44.5	110.0	0.055	52
			0.280	23.0	59.0	262.0	0.145	70
SBR-15495	2	1470	0.510	24.5	33.5	54.3	0.028	40
			0.486	24.5	33.5	85.5	0.042	45
			0.461	23.5	45.5	116.0	0.059	53
			0.436	23.0	34.5	149.0	0.076	44
SBR-15496	2	1740	0.484	23.8	33.0	49.0	0.018	33
			0.434	23.2	33.5	84.0	0.037	37
			0.383	23.0	34.0	163.0	0.083	46
			0.335	23.0	34.0	268.0	0.146	45
SBR-15497	2	2500	0.432	25.0	33.0	23.8	0.006	20
			0.382	24.5	33.0	54.8	0.018	25
			0.332	24.0	34.0	106.0	0.044	32
			0.282	23.5	35.0	173.0	0.090	40
SBR-15620	3	1375	0.530	23.0	33.0	60.0	0.032	50
			0.505	23.2	33.0	86.0	0.054	55
			0.480	23.0	33.0	129.0	0.666	48
			0.455	22.5	33.5	159.0	0.083	54
SBR-15621	3	1820	0.499	24.0	32.0	53.7	0.033	50
			0.458	22.5	45.0	81.3	0.051	65
			0.419	24.0	46.0	112.0	0.078	70
			0.378	22.5	46.5	177.0	0.118	74
			0.329	21.5	46.0	298.0	0.194	70
SBR-15622	3	2200	0.458	23.8	41.5	43.4	0.021	55
			0.438	24.5	32.5	55.7	0.029	44
			0.399	23.0	32.5	80.7	0.053	55
			0.372	24.2	33.0	116.0	0.075	55

* Specific surfaces were determined by the A.S.T.M. turbidimeter method but were corrected for surface contributed by >325-mesh material. The correction was significant only for the coarser cements.

Table 18 (Concluded)

Cement No.	Clinker No.	Specific Surface cm^2/gm	Cement Content of Paste c	Paste Temp., $^{\circ}\text{C}$	Height of Paste, mm	Bleeding Rate $Q \times 10^6$	Bleeding Capacity, ΔH^1	Bleeding Time, min.
SBR-15622	3	2200	0.351	23.8	33.0	130.0	0.087	55
			0.322	22.5	47.5	206.0	0.139	--
			0.298	23.8	35.0	289.0	0.166	55
SBR-15667	4	1250	0.500	24.0	33.0	109.5	0.069	--
			0.475	22.8	33.0	128.0	0.083	--
			0.450	22.5	34.5	177.0	0.094	--
			0.425	23.5	34.0	230.0	0.128	--
SBR-15762	4	1500	0.490	22.8	32.5	89.0	0.056	50
			0.460	23.5	34.0	144.0	0.080	60
			0.430	22.5	33.5	168.0	0.102	60
			0.400	23.0	34.0	256.0	0.145	60
SBR-15763	4	1800	0.450	23.3	32.5	109.0	0.072	57
			0.425	23.8	33.5	144.0	0.094	64
			0.400	23.3	34.0	180.0	0.113	60
			0.375	22.8	34.2	231.0	0.117	60
SBR-15669	4	2290	0.426	24.0	42.0	83.3	0.056	--
			0.397	24.2	32.5	97.8	0.069	--
			0.357	23.0	44.5	153.0	0.126	--
			0.327	23.6	34.5	197.0	0.164	--
SBR-15696	5	1305	0.480	24.0	33.5	108.0	0.055	45
			0.460	24.5	34.0	154.0	0.076	50
			0.440	23.5	35.5	189.0	0.097	45
			0.420	24.3	34.5	229.0	0.113	45
			0.400	23.0	33.2	310.0	0.138	46
SBR-15760	5	1500	0.450	23.7	34.0	104.0	0.056	53
			0.400	23.6	34.5	180.0	0.118	55
			0.375	23.7	35.0	265.0	0.151	55
			0.350	22.8	35.5	350.0	0.187	55
SBR-15761	5	1800	0.450	24.6	33.2	67.0	0.042	58
			0.400	23.8	34.0	107.0	0.075	60
			0.400	23.1	41.3	116.0	0.090*	75
			0.350	23.4	35.5	202.0	0.147	65
			0.325	23.4	35.2	251.0	0.180	--
SBR-15698	5	2265	0.450	23.8	33.0	34.8	0.021	50
			0.400	23.5	33.0	66.0	0.066**	--
			0.350	23.3	35.0	118.0	0.105	72
			0.300	23.7	35.0	205.0	0.178	80

*Result of two tests which showed 0.089 and 0.091.

**A check test showed 0.060.

Appendix C

Additional Study of Equations 2 and 5

The corrections for immobile liquid that are made in Equations 2 and 5 differ in one respect that is not discussed in the main text. This is, in deriving Equation 5 from Equation 3 the quantity that was assumed to

represent immobile liquid, namely $\frac{w_i}{1 - w_i} c$, was sub-

tracted from w and was added to c , whereas in the derivation of Equation 2 only the w was corrected for immobile water. It follows that the two equations would differ in form even if equivalent assumptions were made as to the quantity of immobile water. It is the purpose here to show why the new approach to the problem requires the addition of the immobile water to c , and to show that a corresponding modification of Equation 2 would not conflict with the method of derivation originally used in Bulletin 2.

Equation 3, from which Equation 5 was derived, has been shown elsewhere (15) to be the same as

$$Q = 0.123V_s \cdot \frac{w^3}{c} \quad (9)$$

where V_s is the velocity obtained by applying Stokes' law expressed in terms of σ (rather than particle-radius), irrespective of whether the particles are of uniform size or not. It thus embodies the effects of all dimensional quantities. The rest of the right-hand member of Equation 9 shows how V_s is modified by the relative proportions of settling bodies and mobile liquid. Since V is determined by sedimentation analysis, it is

correct whether or not the solid particles carry liquid with them*. But liquid that accompanies the particles cannot be considered a part of the mobile liquid. It functions, instead, as a part of the settling bodies. Hence, to represent correctly the effective volumes of settling and nonsettling constituents, both c and w must be corrected for any immobile liquid, as was done in the derivation of Equation 5.

In deriving Equation 14 of Bulletin 2, which is the same as Equation 2 of this report, the c was not corrected because it entered the equation simply as the factor by which the specific surface was multiplied in order to obtain the surface exposure per unit volume of paste. Indeed, from the viewpoint that was adopted, the c should not have been corrected, but the specific surface should, theoretically, have been corrected instead. Actually, in Bulletin 2 the specific surface was not corrected but was used as a first approximation to the correct surface, a procedure which appeared to be justified by the results. However, to make the rate equation conform strictly to current theory the correction is needed, and it can be made as explained below.

The studies that have now been made indicate that angular particles can be treated as spheres of solid plus immobile liquid. It is not supposed that the particles with their accompanying liquid actually have true spherical shapes, but they act very much as though they did. Now, the specific surface σ which is used in Equation 2 is calculated from Stokes'^w law as though the particles were spheres, but the difference in density of the spheres and the liquid is assumed to be $(d_c - d_f)$.

*This is true for inert particles. If there is chemical reaction, the use of a different liquid in the sedimentation-analysis may make an appreciable difference. The present treatment neglects any such difference but does not differ in this respect from the treatment in Bulletin 2.

This makes no allowance for the fact that a "sphere" is not all cement but contains $\frac{w_i}{1 - w_i}$ parts of liquid

to one part of solid. (In this development the immobile liquid is calculated in the same way as it was for Equation 5.) The correct density difference for the spheres is

$$\frac{d_c + \frac{w_i}{1 - w_i} d_f}{1 + \frac{w_i}{1 - w_i}} - d_f,$$

or $(1 - w_i)(d_c - d_f)$. Use of this density difference instead of $(d_c - d_f)$ in Stokes' law gives $\sigma_w \sqrt{1 - w_i}$

for the specific surface of the spheres, if σ_w is calculated the same as for Bulletin 2. But $\sigma_w \sqrt{1 - w_i}$ is

not the surface exposure per unit volume of cement, but per unit volume of spheres. Per unit volume of cement the surface is $\sigma_w \sqrt{1 - w_i} \left(1 + \frac{w_i}{1 - w_i}\right)$ or $\frac{\sigma_w \sqrt{1 - w_i}}{1 - w_i}$.

The square of this, $\frac{\sigma_w^2}{1 - w_i}$, should therefore replace

σ_w^2 in Equation 2. The result is then the same as if σ_w^2 were left unchanged and $\frac{c}{1 - w_i}$, which is $c + \frac{w_i}{1 - w_i} c$,

were used in place of c as was done in developing Equation 5. To conform to the assumption that the immobile water is $\frac{w_i}{1 - w_i} c$, $\frac{w_i}{1 - w_i} c$ instead of simply w_i should

be subtracted from each w of Equation 2. With these changes Equation 2 becomes the same as Equation 5 except for the value used for the empirical proportionality constant and the symbol used for the specific surface. (The σ is assumed to be accurate whereas in obtaining σ_w the portion of the sample in which the particles are less than $7\frac{1}{2}$ microns in diameter is not analyzed.)

Some difference between Equations 2 and 5 might perhaps be expected to result from the fact that in Bulletin 2 the buoyancy of the falling particles was treated as equal to the weight of the displaced water whereas in the derivation of Equation 5 it was shown to be greater and was therefore differently evaluated. However, the buoyancy was not actually needed in the development according to Bulletin 2. Over unit base area the weight of cement in excess of the weight of an equal volume of water was called the weight in excess of the buoyancy, but it was used, correctly, as the excess hydraulic pressure.

Appendix D

Mathematical Developments with Respect to Bleeding Capacities

Derivation of Equation 6 of Section 2

Equation 6 expresses mathematically the hypothesis presented in Bulletin 2 (p. 65) that a cube of paste will settle until the height is the same as that of a cube having a volume equal to the limiting, or base, volume of the cement in the paste. This can be shown as follows:

Let the height of the cube of paste be 1. After settlement, the height will be $1 - \Delta H'$. The initial volume is 1, the base volume is $(1 - \Delta H')^3$, and the volume of cement is c . Let the volume of cement per unit of base volume be represented by c_B . Then $c_B = \frac{c}{(1 - \Delta H')^3}$ or $c = c_B (1 - \Delta H')^3$, which is Equation 6.

The Assumed Linear Relationship between $\sqrt{\Delta H'}$ and w , for Coarse Cements

The fact that for coarse cements the linear relationship between $\sqrt{\Delta H'}$ and w holds at practically all possible concentrations suggests that the relationship represents approximately the fundamental law governing the bleeding capacities of such cements. Consequently, a study of this relationship is presented here.

The equation that represents the relationship is readily derived from the fact that the straight line passes through the points (1,1) and ($w_B, 0$), where w_B is the volume of water in a unit of base volume.* Thus, the

*The base volume that is here considered is the minimum volume indicated by the assumed linear relationship between $\sqrt{\Delta H'}$ and w . It differs somewhat from the base volume indicated by equation 6.

slope is $\frac{1}{1 - w_B}$; and the equation is

$$\sqrt{\Delta H'} = \frac{w - w_B}{1 - w_B}$$

Since $w = 1 - c$ and $w_B = 1 - c_B$, the equation may also be written

$$\sqrt{\Delta H'} = \frac{c_B - c}{c_B} = 1 - \frac{c}{c_B}$$

The next point that will be examined is the relationship between the paste concentration and the settled volume per unit volume of cement. This latter quantity is $\frac{1 - \Delta H'}{c}$. But, from the above equation

$$\Delta H' = \left(1 - \frac{c}{c_B}\right)^2 = 1 - \frac{2c}{c_B} + \frac{c^2}{c_B^2}$$

Hence,

$$\frac{1 - \Delta H'}{c} = \frac{2}{c_B} - \frac{c}{c_B^2} \quad (10)$$

Thus the settled volume per unit. of cement decreases linearly with c , and since $c = 1 - w$ it increases linearly with w .

A somewhat different insight into the significance of Equation 10 may be developed by rearranging the equation as follows:

$$\frac{1 - \Delta H'}{c} = \frac{1}{c_B} + \frac{1}{c_B} \left(1 - \frac{c}{c_B}\right)$$

$$1 - \Delta H' = \frac{c}{c_B} + \frac{c}{c_B} \left(1 - \frac{c}{c_B}\right)$$

$$\frac{(1 - \Delta H') - \frac{c}{c_B}}{1 - \frac{c}{c_B}} = \frac{c}{c_B} \quad (11)$$

To see the significance of Equation 11, note that since $1/c_B$ is the base volume per unit volume of cement, c/c_B is the base volume per unit volume of initial paste, $1 - c/c_B$ is the water in excess of "base" water in a unit of initial paste, and $(1 - \Delta H') - c/c_B$ is the amount of this excess water that remains in the settled paste. Accordingly, Equation 11 shows that the proportion of the "excess" water that is retained in the paste is the same as the proportion of the initial volume that can be considered "base" volume. See the closing part of section 3 for other ways of expressing this.

Appendix E

The Measurement of Bleeding of Pastes

On the basis of the principles stated in Bulletin 2 and the experience gained in later work, a generally reliable procedure for determining the bleeding characteristics of pastes can be outlined. If the test is made as described, at a cement concentration at which the paste can be poured easily but has sufficient coherence to avoid "channeling" during test, the bleeding rate and bleeding capacity will nearly always conform to Equations 2 and 7 which are reproduced here.

$$Q = \frac{0.2g(d_c - d_f)}{\sigma_w^2 \eta} \cdot \frac{(w - w_i)^3}{c} \quad (2)$$

$$\Delta H' = k^2 c [w/c - (w/c)_m]^2 \quad (7)$$

The experimental constant w_i of Equation 2 can be determined from one bleeding test, but tests at two different concentrations are required to determine the two experimental constants, k and $(w/c)_m$ of Equation 7. Tests at three or more concentrations covering a range of 0.1 or more in the value of c are desirable, in order to avoid long extrapolations in estimating results for other concentrations, and to test the accuracy of the equations. (See Table 18 for suitable concentrations.) The equations will generally represent bleeding data with about the precision with which the data can be duplicated. However, neither equation should be regarded as strictly precise. Equation 2 is only partly theoretical and embodies practical approximations discussed in section 2; Equation 7 is wholly empirical.

Lack of agreement with the equations will be indicated if data for several different concentrations cannot be represented adequately by straight lines on plots of $(Qc)^{1/3}$ versus w , and $\sqrt{\Delta H'/c}$ versus w/c . Indeed, in the former case, the slope of the line must also agree with a calculated value. (See later.) Small discrepancies

are to be expected, but when materially different results are obtained the cement may be one that requires longer mixing in order to give "normal" results. If the paste tends to set quickly, normal results might perhaps be obtained at a lower paste height. If discrepancies of important magnitude persist after careful checking, it is obviously best to use the experimentally obtained curves in making predictions. However, if the testing is properly done, very few cases of this kind are likely to be found.

The method of test follows:

Suitable Equipment:

Spatula

50 or 100 ml glass graduate

250 ml glass graduate

Thermometer, 0 to 100°C, graduated to 1°

Balance, reading to 0.5 gm or better

Electrical kitchen mixer, with one-quart mixing bowl.

Lid for the one-quart mixing bowl, made so that it can be placed during mixing. It should have a slot (with cover strip) to admit the shafts of the stirrers, and a hole through which a thermometer can be inserted.

Cylindrical jar to contain the paste during test. Suitable dimensions are 4-in. diameter (about 10 cm) and 3-in. height. The jar may be either glass or metal, but the walls must be rigid and the bottom flat.

Gage for measuring the initial height of the paste. A straight length of wire used as a probe can afterward be read against an ordinary scale to an accuracy of about 0.5 mm. A gage giving greater precision can be constructed from a vernier caliper.

The caliper is mounted vertically (with jaws at top) on a T-frame that can be laid on top of the test jar. The main scale of the caliper is made immovable with respect to the T-frame. A guide strip which moves with the movable jaw is tipped with a small flat metal plate which is brought into contact with the surface of the paste. With this device the level of the paste can be read to 0.1 mm. For a 40 mm depth of paste the precision is 1/4%.

Float for use on the paste. A disk of bakelite or lucite 20 to 25 mm in diameter and about 2 mm thick can be used for the main body of the float. A thread of glass about 3-in. long is mounted vertically at the center of this with a bit of wax. (Alternatively, a fine wire can be used, but the weight of the float divided by the volume of the disk must be less than the density of the paste.)

25-power microscope (with cross-hair in eyepiece) mounted horizontally and equipped for vertical movement over a 20-to 30 mm range with provision for reading elevation to 0.001 mm. Such an instrument has ample accuracy and is obtainable, completely equipped, from precision-instrument companies. However, bleeding rates can be obtained to an accuracy of about 1% by using 5x magnification and reading to 0.005 mm.

A stop-watch, or laboratory timer. An ordinary watch with a second hand can be used but is less convenient.

Light source against which to view the end of the float-stem with the microscope. This may be a 10-watt lamp with a piece of paper for a diffusing screen. Avoid high-wattage lamps which heat the paste unnecessarily.

300-ml Erlenmeyer flask, if density of cement in water is to be determined (see later discussion).

Preparation of Paste

A height of paste of 40 to 50 mm appears to be most satisfactory.* In a jar 10 cm in dia. the corresponding volume of paste will be about 300 to 400 ml. Assuming 350 ml, the amounts of water and cement needed are 350w ml and 350cd_c grams, respectively.

It is desirable to run all tests at a constant temperature. If the laboratory temperature is not controlled, tests can still be run at a constant temperature by taking suitable steps to minimize heat transfer. Most of the tests at the P.C.A. Research Laboratory have been made at 23-24°C. The mix water should be at a lower temperature, determined by experience, so that after mixing the paste-temperature will be within $\pm 1^\circ\text{C}$ of the chosen test temperature.

Place the water in the one-quart mixing bowl and add the cement while the stirrers are turning at low speed. Use the spatula to bring into the mix any cement that clings to the sides of the bowl either above or below the fluid line. Put the lid in place and run the mixer at full speed for 2 minutes. Allow the paste to stand for 3 minutes and then mix at full speed for 2 more minutes.

*Use of such heights will sometimes result in total bleeding-times that exceed the apparent "dormant" period, but experience has shown that the estimated dormant period can be considerably exceeded without much affecting $\Delta H'$. This is reasonable because only the density of the sediment last laid down is affected. Paste heights of 20 mm are too low and give low results, both for Q and $\Delta H'$. A 30 mm height is much better, but the results still tend to be a little low, especially the value of $\Delta H'$.

During mixing, keep the bowl turning slowly. Take the temperature of the paste shortly before shutting off the mixer.

After the mixer is shut off, keep the paste stirred with the spatula, or a spoon, and transfer it as quickly as possible to the test-jar. Start the timer and immediately measure the height of the paste. If a plumb wire is used, lower it vertically into the paste and rotate it a bit after it touches bottom. Then lay it aside and measure the coated length later with a millimeter scale.

Measurement of Bleeding

Place the jar of paste in front of the microscope and pour water from the small graduate* down the side of the jar till it forms a layer over the surface of the paste. Submerge the float-disk in the water at the center and let it down upon the surface of the paste. If the disk does not wet readily, a pencil can be used to force it under the surface of the water. After releasing the float, jar the vessel to seat the float properly.

Place the light-source back of the test-jar, focus the microscope on the tip of the float-stem, and set the cross-hair for a scale reading. Take readings at one- or two-minute intervals during the period of constant bleeding rate. Thereafter, readings at five-minute intervals are sufficient to determine the shape of the bleeding curve. When only the initial bleeding rate and the bleeding capacity are of interest, readings need be taken only at 10 or 15-minute intervals after the initial rate has been established.

*A bottle of water, mounted at slight elevation and discharging from a bottom outlet through a length of rubber tubing, is a convenience if many tests are made.

After each scale reading, the difference from the immediately preceding reading and from the initial one can be figured and entered in the record. The difference from the initial reading is a convenient value to plot. Differences between successive readings show how constant the rate is and enable the end of the initial constant-rate period to be determined.

The Bleeding Data

The initial bleeding rate that remains constant for some 10, 20, or more minutes at the start is the Q of Equation 2. It is best determined from a plot of the change in height of paste versus time. Occasionally, the first one or two points are a little out of line, in which case they should be disregarded. The straight line whose slope gives the value of Q is extended to the zero of the time-scale, and the total settlement is figured from this zero position. This total settlement divided by the initial height of the paste gives the bleeding capacity $\Delta H'$.

The w_1 of Equation 2 is determined from a plot of $(Qc)^{1/3}$ versus w . The equation indicates that the data-points should fall along a straight line which cuts the axis of w at w_1 . The theoretical slope of the line is the cube-root of $\frac{0.2g(d_c - d_f)}{\sigma_w^2 \eta}$. The data-lines are

always drawn to the theoretical slope except when there are obvious discrepancies of significant magnitude.

The constant k of Equation 7 is the slope of the data-line in a plot of $\sqrt{\Delta H'/c}$ versus w/c . The constant $(w/c)_m$ is the value of w/c where the line crosses the w/c -axis. Both constants are determined empirically by drawing the line that best represents the experimental data.

Having determined these constants for a given cement, Equations 2 and 7 can be used to estimate the values of Q and $\Delta H'$ at paste concentrations not tested experimentally. Of course, for concentrations intermediate between ones tested experimentally, rather good predictions can be made directly from plots of Q versus w , and $\Delta H'$ versus w . Semi-logarithmic paper can be used to obtain approximately linear curves by plotting the Q and $\Delta H'$ values on the log scales.

Cement Density

In Equation 2, d_c is the density of cement as determined in water. This density is used directly in the equation and also in the calculation of c , though not in calculating σ_w which is the product of the surface area per gram (by Wagner turb.) and the cement density as determined in kerosene in the usual way. The use of two different determinations of cement density is a refinement that is not strictly necessary in practical work. Equation 2 already involves other approximations (see section 2); and the use throughout of the density as determined in kerosene--or, indeed, just an average cement density--would not make a large difference in the results. However, a relatively simple determination of the apparent density of cement in water can be made as follows:

Use proportions of cement and water appropriate for a bleeding test and such as do not cause appreciable entrainment of air. Mix as for a bleeding test, taking care that the final temperature shall be approximately room temperature. Pour the paste into an Erlenmeyer flask of nominal 300 ml capacity and obtain level measure.*

*A small, flat glass plate can be used to strike off excess paste and can also be used as a cover. It can be made close-fitting by grinding it against the rim of the flask with a little moistened abrasive powder prior to use.

The total volume of the flask should be known accurately, and this volume, in cc, should be divided by the weight of the paste in the flask in grams to obtain the density of the paste, d_m . From the quantities used in the mix calculate the ratio, r , of the weight of cement in grams to the volume of water in cc. Then

$$d_m = wd_f + rw, \text{ or } w = \frac{d_m}{r + d_f}$$

and

$$d_c = \frac{rw}{1 - w} = \frac{rd_m}{r + d_f - d_m}$$

The apparent density of cement as determined in water is a little greater than the density as determined in kerosene because interaction between the cement and the water decreases the total volume of the system. (See section 7.)

